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VOL. I

# PRACTICAL CHEMISTRY

D.P. GOEL & V.C. GARG

PITAMBAR PUBLISHING COMPANY

+2

# PRACTICAL CHEMISTRY

(Vol. I for Class XI)

*[Strictly according to the New Syllabus Prescribed by the Central Board of Secondary Education, New Delhi in Practical Chemistry for Class XI]*

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# PREFACE

This laboratory manual is intended for class XI students. This book is the result of many years of experience the authors acquired in teaching chemistry.

Each laboratory work is preceded by a brief theoretical introduction for independent study before the student proceeds to perform practical work in the laboratory. At the end of each unit, oral questions with their answers, have been included. It is an integral part of the laboratory work. Numerous diagrams have been given. These diagrams present most of the laboratory exercises in visual terms. Effort has been made to keep pace with the advances in laboratory work.

Care has been taken over the planning of each experiment so as to present the procedure, conclusion, etc. vividly. The subject matter and the experiments have been planned with a view to help the students of all levels.

It is our hope that it will meet the requirements of the students. We look forward to valuable suggestions from all our readers for further improvement of the book, as we earnestly believe in the following words from the Rigveda,

"Let noble thoughts come to us from every side".

We are very much grateful to our colleagues Dr. Mohan Katyal (St-Stephen's College, Delhi), Dr. K.L. Kapoor (Hindu College Delhi), Dr. V.B. Aggarwal (Hans Raj College, Delhi), Sh. I.S. Arora (Modern School, New Delhi) for fruitful discussions and suggestions.

D. P. GOEL
V. C. GARG

# SYLLABUS

## CLASS XI (PRACTICALS)

| | | |
|---|---|---|
| One Practical Paper | 3 hours | 30 Marks |
| (*i*) Core Experiments | | Distribution of Marks |
| (*a*) Content Based Experiments | | 4 |
| (*b*) Volumetric Analysis | | 6 |
| (*c*) Mixture Analysis | | 10 |
| (*ii*) Investigatory Project | | 5 |
| (*iii*) Class Record and Viva | | 5 |

1. **Basic Laboratory Techniques** :
    - (*i*) (*a*) Cutting a glass tube or glass rod
        - (*b*) Bending a glass tube
        - (*c*) Drawing out a glass jet
        - (*d*) Boring a cork
    - (*ii*) Acquaintance with chemical balance and weight box (setting balance and weighing)
    - (*iii*) (*a*) Preparation of an acid solution of desired normality/molarity from a concentrated one.
        - (*b*) Preparation of solutions to be used as laboratory reagents.
        - (*c*) Preparation of standard solution of oxalic acid
2. Preparation of crystals from an impure sample of any one from the following :

    Alum, copper sulphate, ferrous sulphate obtained from Kipp's waste.
3. Determination of solubility of a solid substance in water at different temperatures and plotting of a solubility curve.
4. (*a*) Determination of pH of some solutions (obtained from fruit juices and acids and bases of different dilutions).
    - (*b*) Study of pH change by common-ion effect in case of weak acids and weak bases.
5. (*a*) Setting up of galvanic cells (such as Daniel Cell) and measure their e.m.f. (using a voltmeter of high internal resistance).
6. Study of the shift in equilibrium between ferric ions and thiocyanate ions by increasing/decreasing the concentration of either ions.

or

Study of the shift in equilibrium between $[Co(H_2O_6)]^{2+}$ and $Cl^-$ by changing the concentration of either ions.

7. Study of reaction rates of any one of the followings :
   (*i*) Reactions of iodide ions with hydrogen peroxide at room temperature using different concentrations of iodide ions.
   (*ii*) Reaction between pottasium iodate $KIO_3$ and sodium. sulphite, $Na_2SO_3$ using starch solution as indicator (The reaction will be conducted at different concentrations and temperatues).

8. Determination of (*a*) heat of solution of calcium chloride, and (*b*) heat of neutralization of the reaction between strong acid (HCl) and strong base (NaOH).

9. (*i*) Determination of the strength of a given sodium hydroxide solution by titrating it against a standard solution of oxalic acid.

   (*ii*) Determination of the strength of a given solution of dilute hydrochloric acid by titrating it against a standard solution of sodium carbonate.

10. Study of intraction of metals (any four) with salt solutions and arranging them according to their activity (to form activity series). Metals and metal salts may be selected from the followings :

    Mg, Zn, Fe, Sn, Pb, Cu, Al and their salts

    (Checking the order of metal in series based on the electrode potential will be desirable).

11. Determination of one cation and one anion from the following (insoluble salts to be excluded).

    **Cation** : $Pb^{2+}$, $Hg^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $As^{3+}$, $Fe^{3+}$, $Al^{3+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Mg^{2+}$, $Ba^{2+}$, $NH_4^+$, $Mn^{2+}$

    **Anions** : $CO_3^{2-}$, $S^{2-}$, $SO_3^{2-}$, $SO_4^{2-}$, $NO_2^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $PO_4^{3-}$, $CH_3COO^-$

12. (*i*) Determination of melting point of a solid substance (perferably an organic substance of low melting point).

    (*ii*) Determination of boiling point of an organic liquid from the followings :

    benzene, acetone, acetic acid, carbon tetrachloride and ethyl alcohol.

13. Detection of nitrogen, sulphur and halogens in an organic compound (detection of two elements may be asked, combination of halogens may be avoided).

14. Preparation of acetylene and study of its acidic character.

□ □

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# UNIT 1

## Basic Laboratory Techniques

### 1.1. Introduction

Chemistry laboratory is an integral part of a course of chemistry. It is necessary for the students to get familiarized with the equipments and permanent fixtures in the laboratory.

Work in a chemical laboratory is effective only when it is performed conscientiously, with an understanding of its theory and basic techniques. Moreover, every chemical operation requires that the experimenter be careful and attentive. Carelessness in handling the apparatus and lack of planning and organization of chemical work may result in serious consequences and incorrect results. This is why students are allowed to work in a laboratory only after preliminary briefing.

### 1.2. Common Laboratory Glass-ware

Experiments are performed in special laboratory ware made from thin or thick glass. The glassware shown in Fig. 1.1 is used the most in chemical laboratories. Ware in which reactions are performed with heating is made from heat resistant glass.

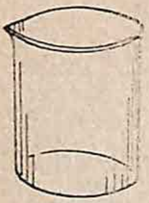
**Beaker.** It is a flat-bottom cylindrical vessel with a pouring tip. It is available in various sizes. It is primarily used for storing the solutions. It can be used for carrying out reactions.

**Desiccator.** It is a specially designed ware made of ordinary glass. It is used for cooling the crucible in dry air to avoid absorption of moistures. Some drying chemicals, such as anhydrous calcium chloride or silica gel is placed in the bottom of the desiccator.

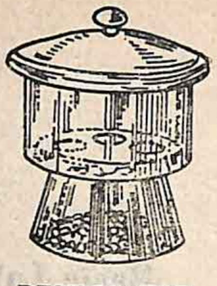
**Flask.** It is a bottle shaped apparatus with a round bottom body and a narrow neck. It is available in various shapes and sizes.

(*a*) *Round bottom flask.* It is primarily used for carrying out reactions at very high temperature, *e.g.*, preparation of certain gases, etc.

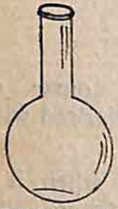
(*b*) *Flat-bottom flask.* It is normally used for carrying out reactions at room temperature, *e.g.*, preparation of certain gases. It is also used for storing solutions etc.



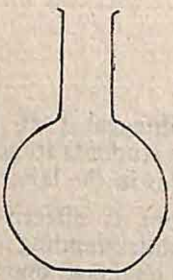
BEAKER



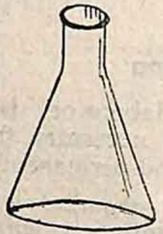
**DESSICCATOR**



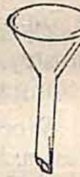
FLORENCE FLASK
(ROUND-BOTTOM
FLASK)



**FLAT-BOTTOM FLASK**



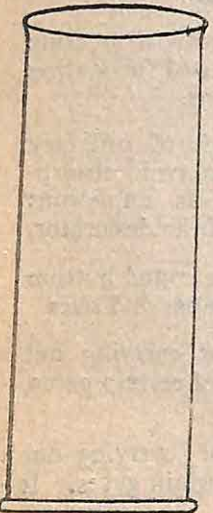
ERLENMEYER FLASK
(CONICAL FLASK)



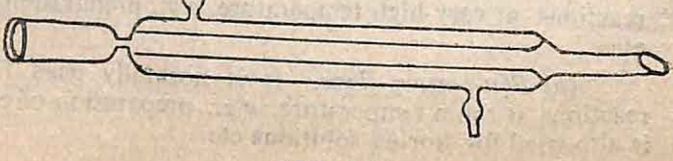
FILTER
FUNNEL

**GLASS TUBE**

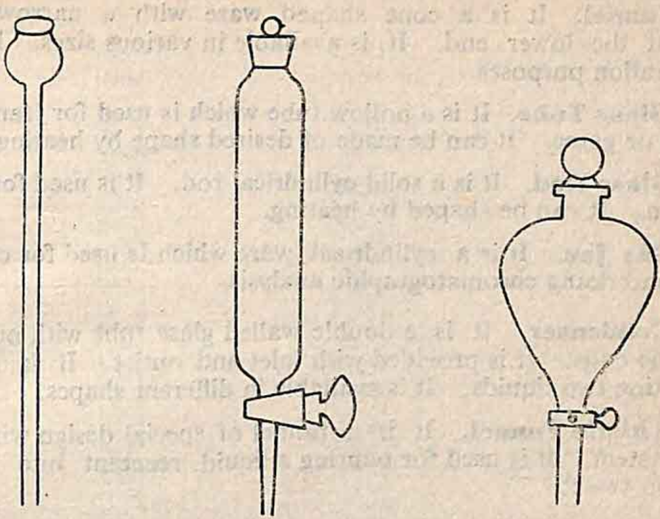
**GLASS ROD**



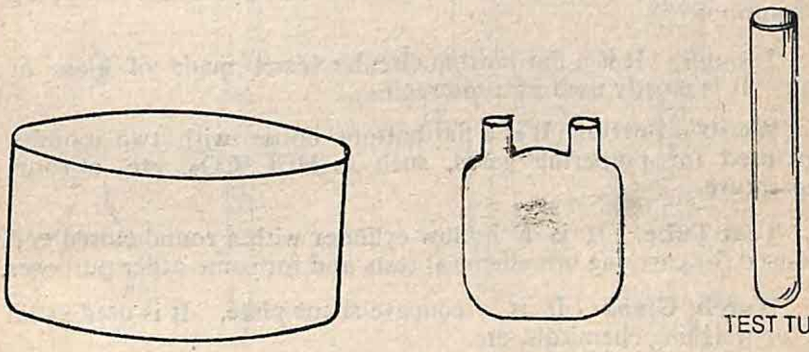
**GAS JAR**



**CONDENSER**

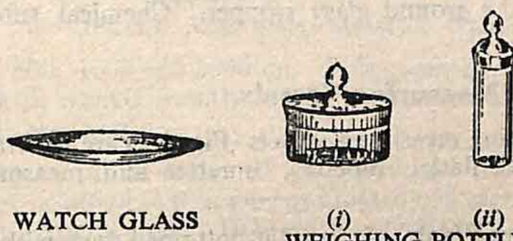


THISTLE FUNNEL (*i*) (*ii*) SEPARATING FUNNELS



TEST TUBE

TROUGH WOULF'S BOTTLE



WATCH GLASS (*i*) (*ii*) WEIGHING BOTTLES

Fig. 1.1. Glass-wares

(*c*) *Conical flask*. It is mostly used for performing volumetric titrations. However, it is at times also used for carrying out some other reactions as well.

**Funnel.** It is a cone shaped ware with a narrow hollow stem at the lower end. It is available in various sizes. It is used for filtration purposes.

**Glass Tube.** It is a hollow tube which is used for transporting liquids or gases. It can be made of desired shape by heating.

**Glass Rod.** It is a solid cylindrical rod. It is used for stirring solution. It can be shaped by heating.

**Gas Jar.** It is a cylindrical ware which is used for collecting gases and doing chromatographic analysis.

**Condenser.** It is a double walled glass tube with opening at both the ends. It is provided with inlet and outlet. It is used for separating two liquids. It is available in different shapes.

**Thistle Funnel.** It is a funnel of special design with a long hollow stem. It is used for pouring a liquid reactant into a sealed reaction vessel.

**Separating Funnel.** It is a funnel with a leak-proof stopper at one end and a stopcock at the other end. It is available in different designs. It is used for separating the two liquids and for dropping the solutions.

**Trough.** It is a flat-bottom circular vessel made of glass or china. It is mostly used as a reservoir.

**Woulf's Bottle.** It is a flat bottom bottle with two mouths. It is used for preparing gases, such as HCl, $CO_2$, etc. at room temperature.

**Test Tube.** It is a hollow cylinder with a round closed end. It is used for carrying out chemical tests and for some other purposes.

**Watch Glass.** It is a concave shape plate. It is used as lid and for weighing chemicals, etc.

**Weighing Bottle.** It is a small glass bottle with flat-ends, straight wall and a ground glass stopper. Chemical substances are weighed in it.

## 1.3. Common Measuring Vessels

The following measuring vessels (Fig. 1.2) are generally used in laboratory work : flasks, pipettes, burettes and measuring glasses/cylinders.

**Measuring Flask.** It is a flat-bottomed flask with a long and narrow neck on which a thin line is marked. It is designed to contain a fixed volume of liquid when filled upto the mark. Since the neck of flask is narrow, a small change in the volume of liquid appreciably changes the position of its meniscus. It is provided with a leak-proof glass stopper. It is available in different sizes, *viz.*, 50,

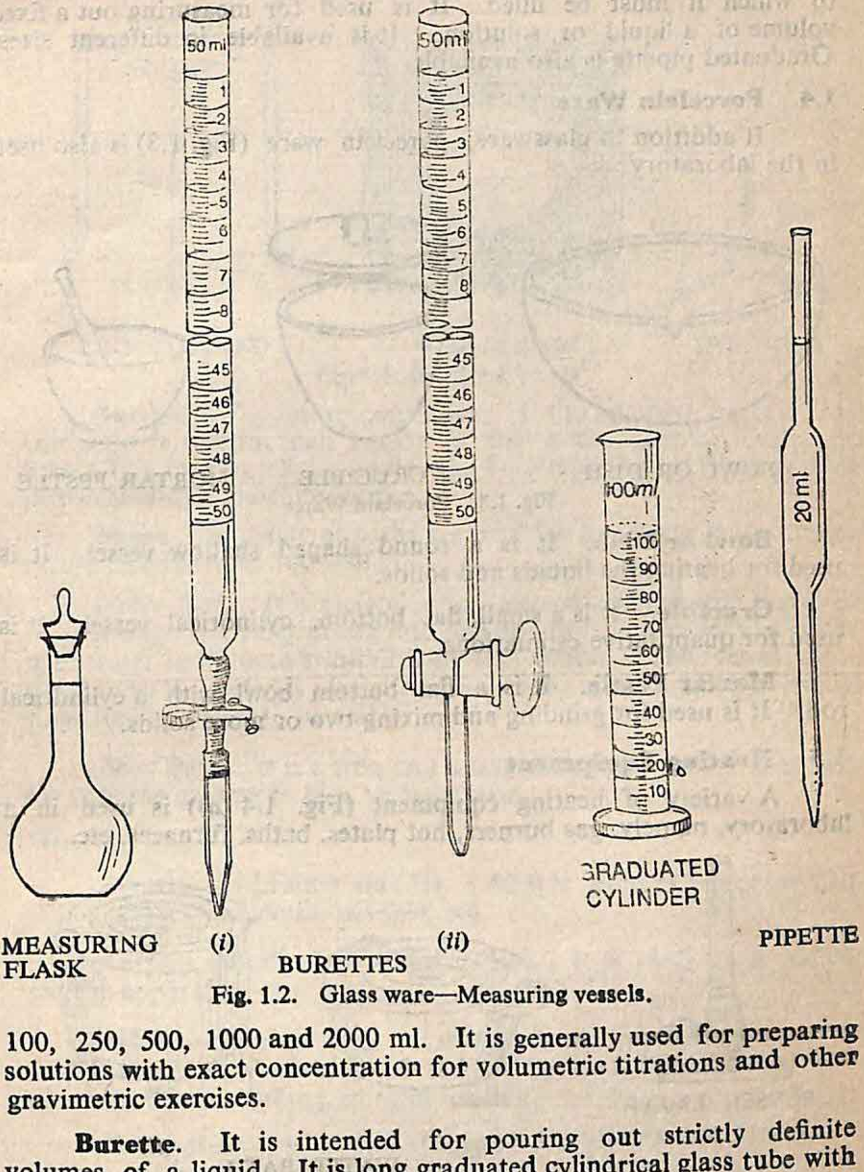


Fig. 1.2. Glass ware—Measuring vessels.

100, 250, 500, 1000 and 2000 ml. It is generally used for preparing solutions with exact concentration for volumetric titrations and other gravimetric exercises.

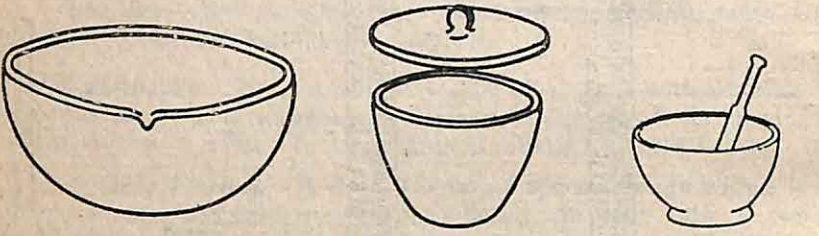
**Burette.** It is intended for pouring out strictly definite volumes of a liquid. It is long graduated cylindrical glass tube with a uniform cross-section. The most popular is 50 ml burette graduated by tenths of a millilitre. The bottom part of a ware is provided with a glass stop cork.

**Graduated Cylinder.** It is used for the rough measurement of liquids and has various capacities, namely 5, 10, 50, 200 ml. etc.

**Pipette.** It is a glass tube with narrow top and bottom ends. The upper portion of the pipette has a mark which indicates the level to which it must be filled. It is used for measuring out a fixed volume of a liquid or solution. It is available in different sizes. Graduated pipette is also available.

## 1.4. Porcelein Ware

It addition to glassware, porcelein ware (Fig. 1.3) is also used in the laboratory.



BOWL OR DISH CRUCIBLE MORTAR PESTLE

Fig. 1.3. Porcelain Wares

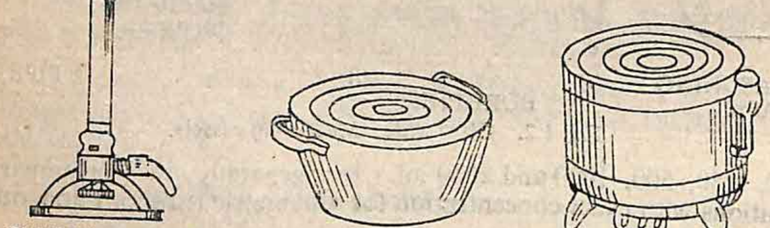
**Bowl or Dish**. It is a round shaped shallow vessel. It is used for heating the liquids and solids.

**Crucible**. It is a small, flat bottom, cylindrical vessel. It is used for quantitative estimations.

**Mortar Pestle**. It is a flat bottom bowl with a cylindrical rod. It is used for grinding and mixing two or more solids.

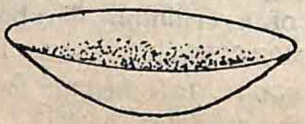
## 1.5. Heating Equipment

A variety of heating equipment (Fig. 1.4 (*a*)) is used in a laboratory, namely, gas burners, hot plates, baths, furnaces, etc.



BUNSEN BURNER

(*i*) WATER BATH (*ii*)



SAND BATH

Fig. 1.4. (*a*) Heating equipments.

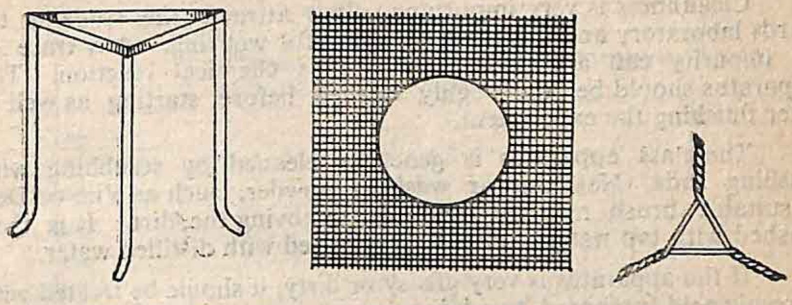

TRIPOD STAND WIRE GUAZE TRIANGLE

Fig. 1.4. (*b*) Heating aids

**Burner**. The most convenient is the Bunsen burner. Air enters the burner through orifice in the lower part of the upper tube. The opening of this orifice can be controlled by rotating *sleeve* provided with a matching orifice.

**Baths**. A variety of baths are used for heating within a temperature interval from 100—300°C :

*Water Bath*. It is a metal vessel covered on top with a number of concentric flat rings fitting into one another. It can be filled either with water or oil upto two-thirds of its volume. The vessel with a solution to be heated is placed on the bath after removing enough rings for the vessel to be stable.

*Sand Bath*. It is a iron pan a tray with clean sand. It is used for carefree heating to high temperatures.

### Heating Aids

A variety of heating aid (Fig. 1.4(*b*)) is used in laboratory, *viz*., tripod stand, wire gauze, triangle, etc.

**Tripod Stand**. It is made of iron. It is used as a support for the apparatus.

**Wire Guaze**. It is a guaze-like fabric of fine wire covered with a thin film of asbestos. It is kept between the flame and the glass-ware for providing uniform heating.

**Triangle**. It is used as a support for heating crucibles etc. It is kept on the tripod stand.

## 1.6. Other Laboratory Aids

In addition to the equipments listed above, some other aids (Fig. 1.5) used in the laboratory are listed below :

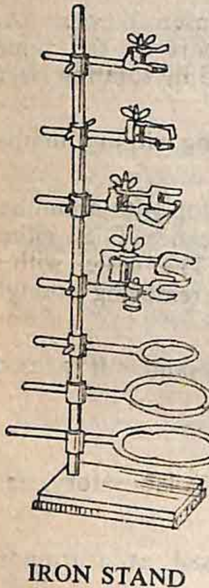
Iron stand, test tube stand, test tube brush, weight box, triangular file, cork, wash bottle, reagent bottle, chemicals, thermometer, filter paper, spatula, tongs, blow pipe, test tube clamp, etc.

## 1.7. Cleaning of Apparatus

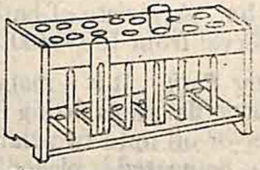
Cleanliness is very important. This attracts the students towards laboratory and fills them with zeal for working. Any trace of an impurity can affect the course of a chemical reaction. The apparatus should be thoroughly washed before starting as well as after finishing the experiment.

The glass apparatus is generally cleaned by scrubbing with washing soda ($Na_2CO_3$) or washing powder, such as Vim or Det. A suitable brush may be used for removing the dirt. It is then washed with tap water. Finally, it is rinsed with distilled water.

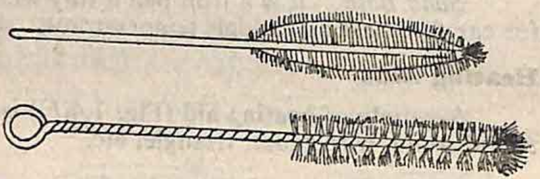
If the apparatus is very greasy or dirty, it should be treated with chromic acid (prepared by adding 5 g of commercially grade potassium dichromate to 100 ml of concentrated sulphuric acid with



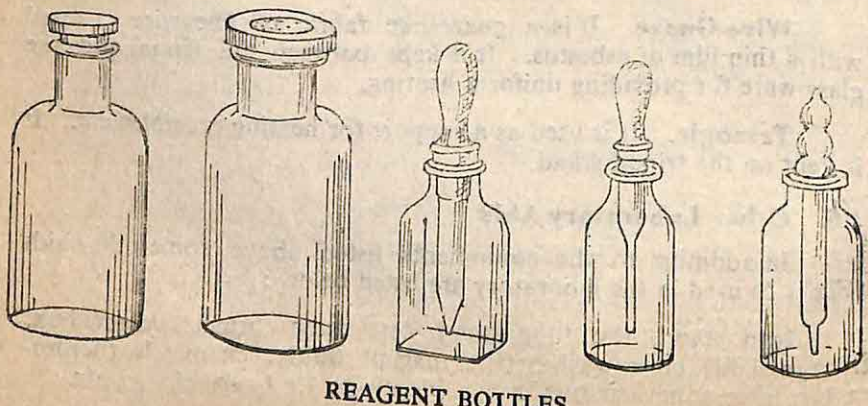
IRON STAND



TEST TUBES AND RACK



TEST TUBE BRUSH



REAGENT BOTTLES

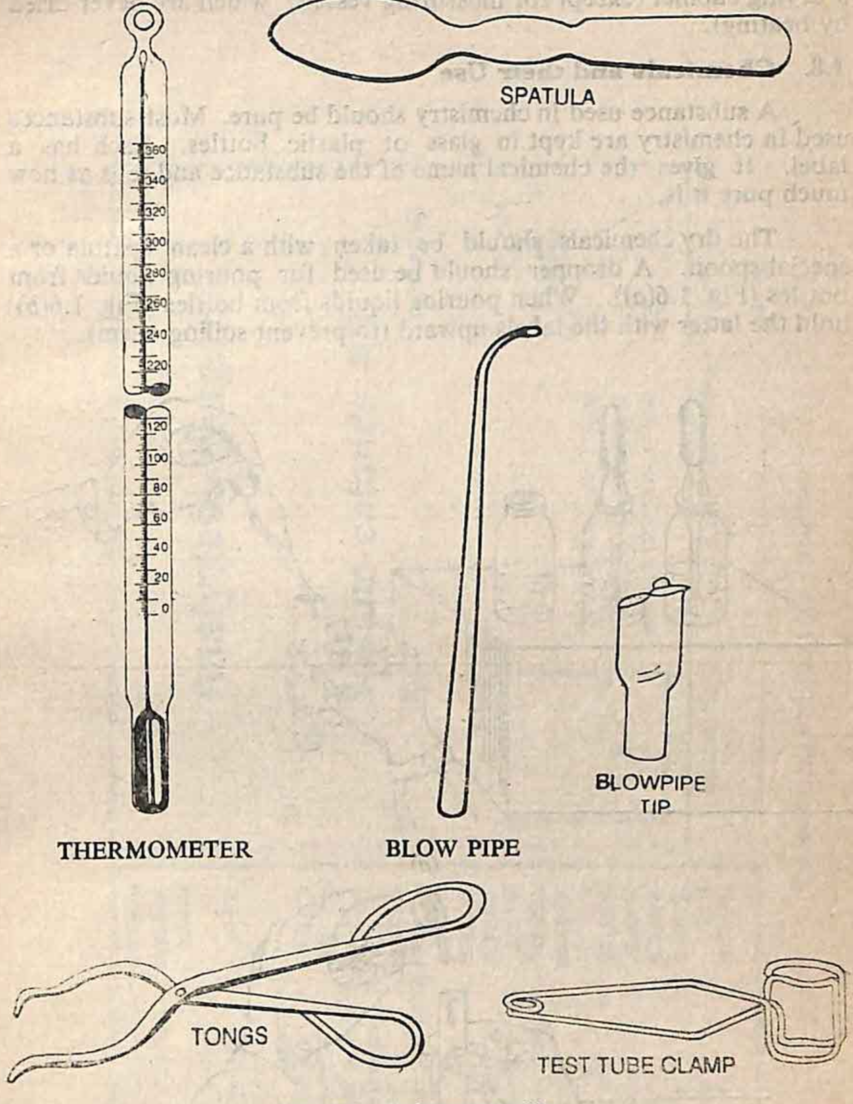


Fig. 1.5. Laboratory aids

stirring and then cooling it). This ensures good wettability of the glass.

After the use, the chromic acid should be poured back into its bottle. The acid is washed away with water.

The washed apparatus should be kept in an inverted position to drain off the water. The inside of the laboratory ware should not be wiped with a towel. When required, the glass ware should be dried in a drying cabinet (except for measuring vessels, which are never dried by heating).

## 1.8. Chemicals and their Use

A substance used in chemistry should be pure. Most substances used in chemistry are kept in glass or plastic bottles. Each has a label. It gives the chemical name of the substance and tells as how much pure it is.

The dry chemicals should be taken with a clean spatula or a special spoon. A dropper should be used for pouring liquids from bottles (Fig. 1.6(*a*)). When pouring liquids from bottles (Fig. 1.6(*b*)) hold the latter with the labels upward (to prevent soiling them).

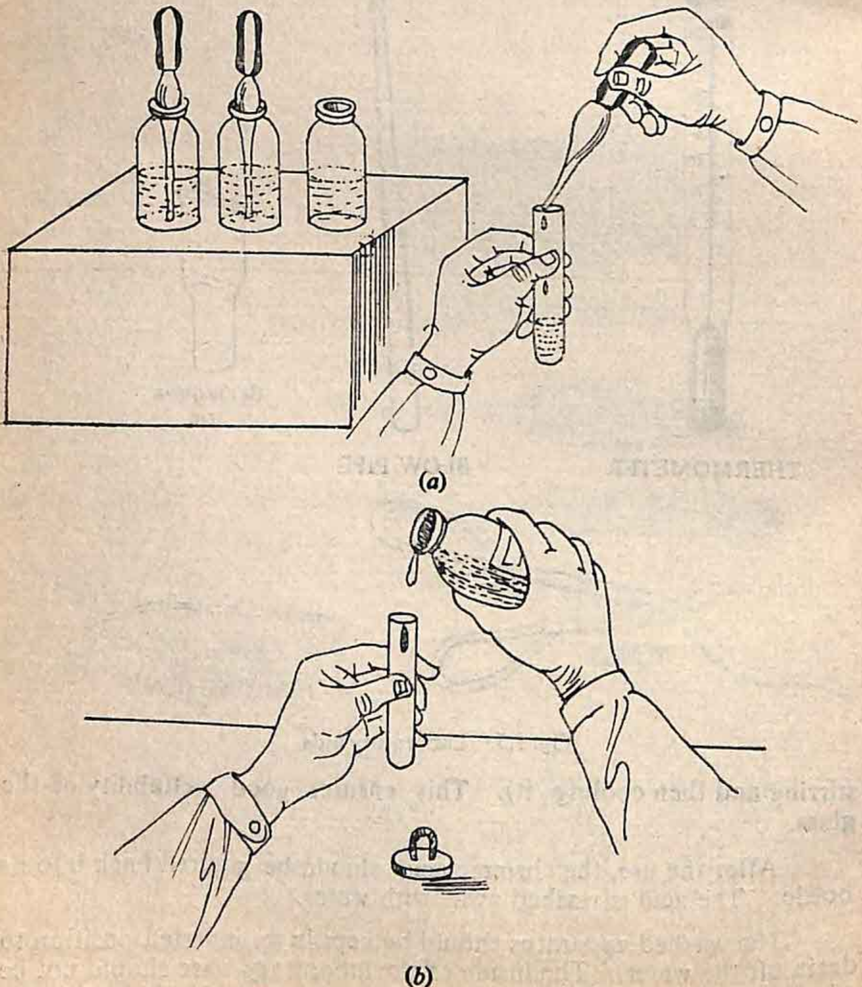
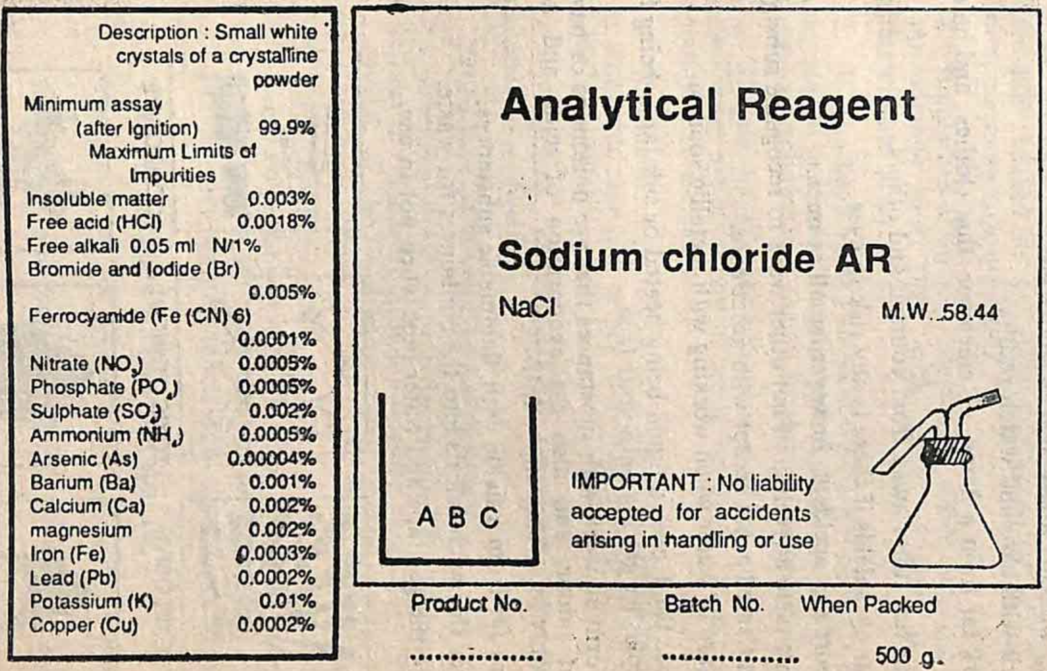


**Fig. 1.6. How to pour reagents.**



Description : Small white crystals of a crystalline powder

| | |
|---|---|
| Minimum assay (after Ignition) | 99.9% |
| Maximum Limits of Impurities | |
| Insoluble matter | 0.003% |
| Free acid (HCl) | 0.0018% |
| Free alkali 0.05 ml N/1% | |
| Bromide and Iodide (Br) | 0.005% |
| Ferrocyanide (Fe (CN) 6) | 0.0001% |
| Nitrate ($NO_3$) | 0.0005% |
| Phosphate ($PO_4$) | 0.0005% |
| Sulphate ($SO_4$) | 0.002% |
| Ammonium ($NH_4$) | 0.0005% |
| Arsenic (As) | 0.00004% |
| Barium (Ba) | 0.001% |
| Calcium (Ca) | 0.002% |
| magnesium | 0.002% |
| Iron (Fe) | 0.0003% |
| Lead (Pb) | 0.0002% |
| Potassium (K) | 0.01% |
| Copper (Cu) | 0.0002% |

**Analytical Reagent**

**Sodium chloride AR**

NaCl M.W. 58.44

A B C

IMPORTANT : No liability accepted for accidents arising in handling or use

| Product No. | Batch No. | When Packed |
|---|---|---|
| ................ | ................ | 500 g. |

The label from a bottle of the purest salt.

## 1.9. Safety

Chemistry is like the dog. There is a chance that it may be dangerous. Always follow the simple rules given below :

Listen carefully to instructions.

Keep working areas clear of books etc.

Work with care and watch results.

Work far from a flame. Remember that clothes and hair will burn.

Point test tubes away from yourself and others.

Wear eyeshields if there is any risk to eyes.

Report any accident, however, small at once.

Don't taste anything. Find other ways to recognize substances.

Don't smell a gas except with great care.

Beware of water when working with metallic sodium.

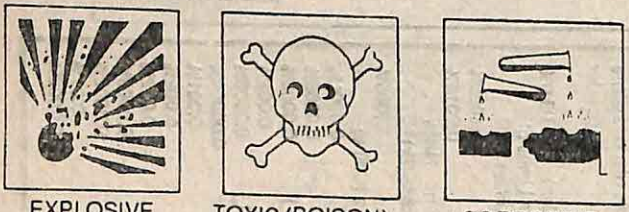
Never bend over a liquid being heated or substance being fused to avoid splashes getting onto your face.

Perform all work with substances that are poisonous or have an unpleasant odour, and also the evaporation of acids and acidic solutions only in a fume-cupboard.

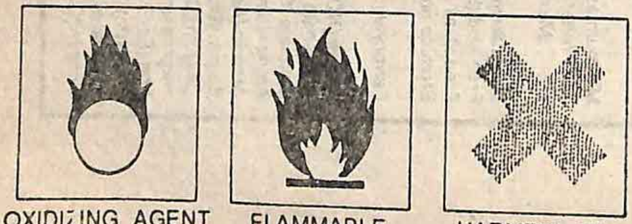
Work far from a flame with flammable substances.

Never throw chemicals into the containers for waste.

Close the gas taps and water taps when not in use.



EXPLOSIVE TOXIC (POISON) CORROSIVE



OXIDIZING AGENT (OXIDANT) FLAMMABLE (WILL BURN) HARMFUL OR IRRITATING

Fig. 1.7. Labels on bottles indicating what the danger is.

The drawings (Fig. 1.7) shown are labels. They are used for dangerous substances. Each picture explains what the danger is. They appear on bottles and containers.

### 1.10. First Aid

1. If a concentrated acid (sulphuric, nitric, etc.) or an alkali solution gets on your skin (hands, etc.) immediately wash the burnt spot under running water for sufficient time. Now apply a cotton wool bandage soaked in an alcohol solution of tannin or a 3% potassium permanganate solution.

2. If splashes of an acid, ammonia, alkali, etc. get into your eyes, immediately wash them with plenty of water and consult a physician without delay.

3. If you have burnt your skin with a hot object, first apply a bandage soaked in an alcohol solution of tannin or a 3% potassium permanganate solution and then a bandage of ointment for burns.

4. If you have cuts with glass etc., first check for any glass piece and then apply a cotton wool bandage. If cuts are strong immediately see a physician.

5. If someone is poisoned by chlorine, hydrogen sulphide or carbon monoxide take him or her out into the open air and immediately call a physician.

6. If someone is poisoned by chemicals, take him or her immediately to a physician.

### 1.11. Procedure of Work in a Laboratory

1. A student must read the description of the experiments he is to perform in the lab from standard texts, acquaint himself with the properties of the substances being studied, with the theory relating to the experiment and also note the special attention that the experiment demands.

2. Every student must keep his table clean and in good order. Only the objects needed for work must be on the table.

3. Never leave reagents taken from the shelves at your place of work.

4. Take dry reagents with a clean spatula.

5. Make use of the dropper for pouring solutions from bottles.

6. Never pour unconsumed reagents back into their storage bottles.

7. Replace caps and stoppers of reagent bottles after use.

8. Use only distilled water when preparing aqueous solutions, washing precipitates rinsing glass-ware and so on.

9. Always wear lab-coats when working.

10. Always follow the instructions given by the teachers.

## 1.12. Laboratory Notebook

A student working in a laboratory has to maintain a complete record of the experimental work done by him. The following points may be kept in mind for an ideal record of the practical notebook :

(*i*) All the pages of the record book should be numbered. Never remove any page from it.

(*ii*) Write the date and the title of the experiment at the top of the right hand page.

(*iii*) Enter your observations directly in the fair notebook. *Never trust your memory in this respect*, it often deceives you. It should never be written on the scraps of paper or filter paper.

(*iv*) Get your readings checked by the teacher before leaving the laboratory.

(*v*) Do not postpone the completion of your practical notebook till the next day. The work should be finished in the laboratory itself.

(*vi*) Mistakes should be crossed out with a single line. Do not erase anything in the notebook.

(*vii*) Write legibly and with good ink.

(*viii*) Always draw diagrams with pencil and on the left hand side of the record book.

(*ix*) Always write a new experiment on a fresh page. It gives a clear idea of the number of experiments done by you.

(*x*) The method employed in performing the experiment is to be written clearly and concisely.

(*xi*) Get your record book signed by the teacher. Keep it clean and tidy.

A example for keeping an experiment records is given below :

**Left hand page**
Date..............
(*i*) Experiment No.
(*ii*) Name of Experiment
(*iii*) Diagram with pencil
(*iv*) Chemical equation (if any)
(*iiv*) Observations
(*v*) Calculations
Result

**Right hand page**
Date..............
(*i*) Experiment No.
(*ii*) Name of Experiment
(*iii*) Apparatus and chemicals
(*iv*) Theory
(*v*) Procedure
(*vi*) Precautions
Result

## 1.13. Study of Burners

There are several types of Bunsen burners, but the working principle in each type is always the same. In a burner, oil or petrol gas is burnt in the presence of air to produce an intense, hot flame. The temperature of the flame can be controlled by regulating the flow of gas and air. The essential parts of a Bunsen burner (Fig. 1.8) are as follows :

(*i*) **Base.** It is a heavy metallic disc made of cast iron or brass. The base keeps the burner in a stable position. It is also provided with a side inlet tube for the gas. The inlet tube is connected by a rubber tubing to the gas tap.

(*ii*) **Nipple.** It is generally made of brass. It is fitted just at the top of the base. It has a fine hole in the centre. The gas which enters the base through the side inlet comes out through the nipple under increased pressure into the burner tube.

(*iii*) **Burning Tube.** It is a long cylindrical tube about 10-15 cm in length. It is generally made of iron or brass. It has two holes opposite to each other above its lower end which serve as *air holes*. It can be screwed or unscrewed at the base. Gas and air enter this tube and burn at the top.

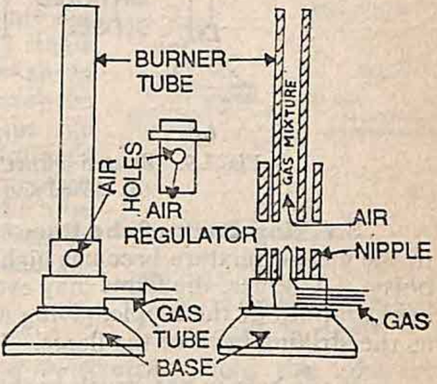


Fig. 1.8. Bunsen burner and its parts.

(*iv*) **Air Regulator.** It is a metallic ring which has two holes corresponding to the two air holes of the burner tube. It is provided at the lower end of the burner tube. By rotating the air regulator, it is possible to control the air holes thus regulating the supply of air.

**Working.** When the burner is to be used, the rubber tubing attached to its base is connected to the gas tap. The air regulator is adjusted to close the air holes. The gas tap is then opened and the lighted match is applied to the edge of the burner opening. The gas burns with a yellow flame, *i.e.*, it is luminous (Fig. 1.9(*a*)). This is caused by the reduced supply of air inside the tube. It is used only for reducing purposes and is, therefore, known as reducing flame.

When the air regulator is adjusted to open the air holes, the flame becomes non-smoky and non-luminous because of the complete combustion of the gas (Fig. 1.9(*b*)). This flame is used for general heating purposes. It has a higher temperature than the luminous flame. It is also known as an oxidizing flame.

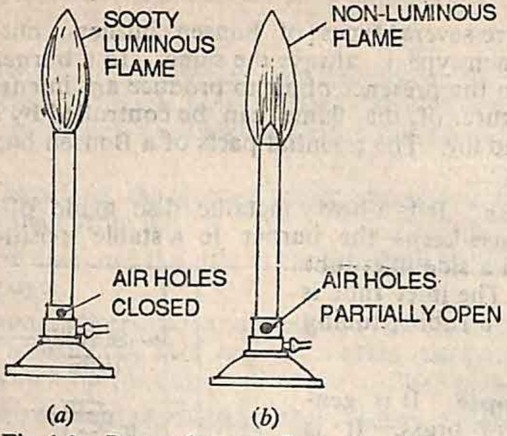


Fig. 1.9. Bunsen burner's flame when holes are (*a*) closed and (*b*) opened.

**Striking Back of the Burner.** When the supply of the air in the gas-air mixture becomes high, the flame becomes unsteady and noisy. At times, the flame may even disappear and the gas burns at the mouth of the nipple, giving a small blue flame. This is known as the striking back of the flame. This makes the burner hot.

If the burner has struck back, close the gas tap, cool it, then light the burner again with a smaller opening for the air.

It is possible to prevent the striking back of the burner by either decreasing the air supply or by increasing the gas supply.

**Precautions.** Whenever a burner is used in a laboratory, the following precautions should be kept in mind :

(*i*) Always keep the air inlets closed when lighting the burner.

(*ii*) To get a steady non-luminous flame, open the air holes gradually.

(*iii*) Regulate the flame by decreasing the supply of gas by adjusting the gas tap.

(*iv*) Always use the non-luminous flame for general heating purposes because it gives the maximum heat due to the complete combustion of the hydrocarbons.

(*v*) Do not throw any chemical into the flame. This enters the burner tube and block the nipple.

(*vi*) When the burner is not in use, put it off by closing the gas tap.

## 1.14. Some Simple Techniques

In a chemical laboratory, all experiments require the fitting up of the apparatus. Quite often this involves cutting and bending of a glass tube, drawing of jets from the glass tube and boring of corks, etc. In this section, we shall describe these simple techniques.

### 1.14.1. Cutting of a glass tube and rounding off its edges

It involves three steps :

(*i*) *Putting a Scratch.* Measure the required length of the tube. Place the glass tube on a flat surface (generally an asbestos sheet placed on the table). Hold the tube in your left hand in such a manner that the thumb points out the place to be cut. Make a single and straight scratch with the sharp edge of a triangular file at the desired place by drawing the file through the full length towards yourself with moderate pressure (Fig. 1.10) while keeping the tube pressed downwards. Do not move the file backward and forward again and again.

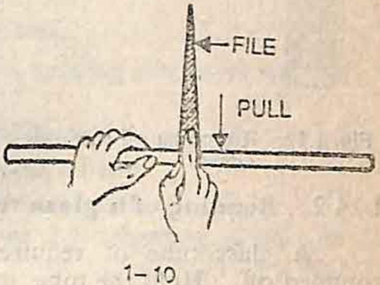


Fig. 1.10. Making a scratch on a glass tube with the help of a triangular file.

(*ii*) *Breaking the tube at the scratch.* Hold the tube in both the hand in such a way that the two thumbs are on either side of the scratch but opposite to each other as shown in Fig. 1.11. Press the tube gently outwards with the help of the thumbs and pull the ends apart at the same time. The tube will break into pieces. If the tube does not break, again make scratch at the same place and break it by the same technique.

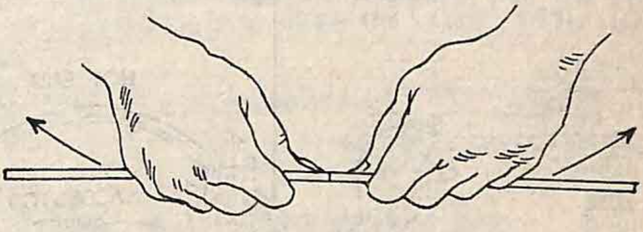


Fig. 1.11. Breaking the tube into two pieces.

(*iii*) *Rounding off the sharp edges.* The freshly cut ends of the tube are sharp and may cause some injury to your hands if used as it is. These are rounded off by rotating the tube in the flame as shown in Fig. 1.12 until it softens a little (the tube should not be heated for a long time otherwise it may get sealed). Now it is cooled in air by placing it on an asbestos sheet. When the edges of the tube are very rough, these are rubbed against a wire guaze before rounding them off.

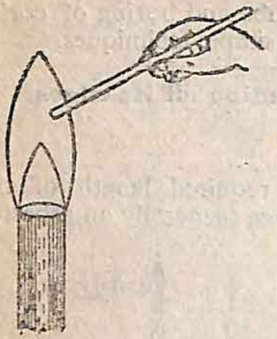


Fig. 1.12. Rounding off the edges.

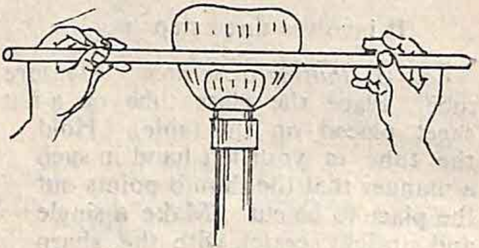


Fig. 1.13. Delivery tube heated and being rotated in a broad flame.

### 1.14.2. Bending of a glass tube

A glass tube of required length is first cut and its edges rounded off. Hold the tube in both the hands and heat the part to be bent into the luminous flame of the fish tail burner (gives a broad flame) while rotating the tube in one direction as shown in Fig. 1.13. When the glass softens and tends to bend by itself, release your left hand and allow the tube to bend by its own weight as shown in Fig. 1.14 until the bend of desired angle is obtained.

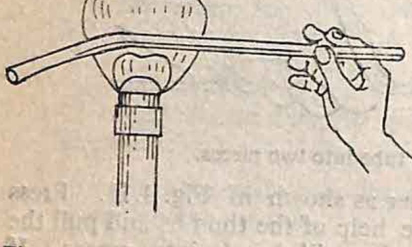


Fig. 1.14. Bending of glass tube under its own weight.

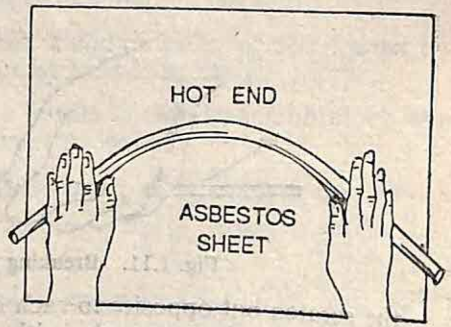
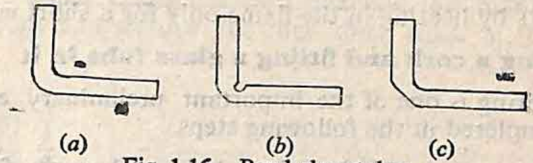


Fig. 1.15. Setting the bend in the same plane.

Hold both the limbs firmly in your hands when the desired angle is reached and place the tube on an asbestos sheet while hot. Press the limbs against the sheet to make them co-planar, *i.e.*, the entire tube touches the asbestos sheet (Fig. 1.15).

Slow cooling (annealing) is necessary to avoid breaking of the tube. Soot deposited on the bent portion should not be removed until it is quite cold.

A properly bent tube (Fig 1.16*a*) should have no folds and constrictions [Fig. 1.16 (*b*), (*c*)].



(*a*) (*b*) (*c*)

Fig. 1.16. Bend glass tubes.
(*a*) Correctly bent
(*b*) and (*c*) Incorrectly bent.

**Precautions.** (1) Tube selected for bending should be neither too thin walled nor too thick walled.

(2) Burner used should give a broad flame.

(3) No force should be used to achieve a bend.

(4) Limbs of the bent tube should be coplanar.

(5) Change of angle of a bent tube by reheating should be avoided.

### 1.14.3. Drawing a jet from a glass tube

Select a delivery tube of suitable diameter and length. Round off its edges.

Hold the tube in both hands and heat the tube in the middle in rotatory fashion. Continue heating until it softens.

Take out the hot tube from the flame and pull the two ends apart slowly and then briskly to draw the jet (Fig. 1.17). Hold the

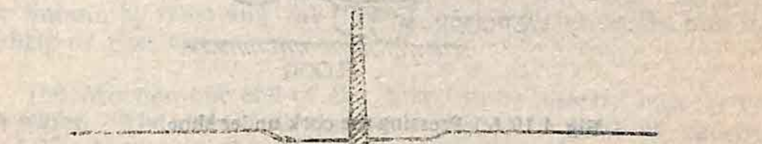


Fig. 1.17. Drawing jet outside the flame.

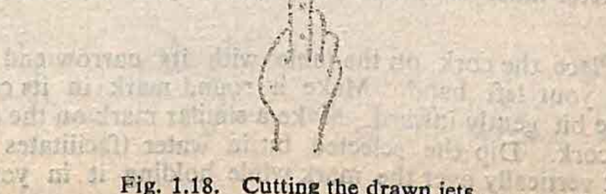


Fig. 1.18. Cutting the drawn jets.

drawn tube in position until it cools down and stiffens. Place it on the table and cut it into two jets by giving a gentle scratch with a triangular file on the capillary portion (Fig. 1.18). Round off the ends of the jets by heating in the flame only for a short while.

### 1.14.4. Boring a cork and fitting a glass tube in it

Cork boring is one of the important preliminary experiments. It may be completed in the following steps.

(*i*) Select a good cork free from holes and cracks for a vessel. It should enter the vessel opening with difficulty. Wet the cork with water and compress it with a cork kneader (press) or by pressing it under shoe (Fig. 1.19), after which it becomes soft and fits well into the opening.

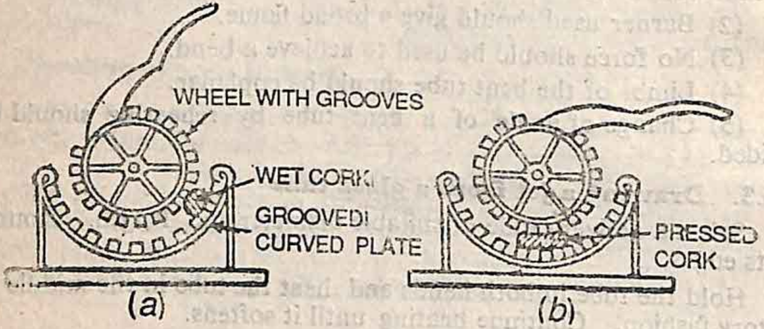


**Fig. 1.19 (*a, b*) Pressing the cork in a cork press.**

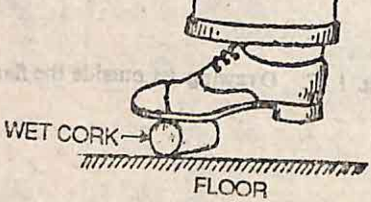


**Fig. 1.19 (*c*) Pressing the cork under shoe.**

(*ii*) Now select a cork borer (bit) of the proper size (Fig. 1.20) whose diameter must be somewhat smaller than that of the glass tube.

(*iii*) Place the cork on the table with its narrow end upward and hold in your left hand. Make a round mark in its centre by pressing the bit gently inward. Make a similar mark on the opposite side of the cork. Dip the selected bit in water (facilitates boring) and place it vertically over the mark while holding it in your right

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hand. Press it downward with a twisting motion (Fig. 1.21). See that the bit and cork axes coincide, otherwise the hole will be skew (Fig. 1.22). When the bit almost reaches the half-way pull out the bit carefully and remove the cork dust stuck in it by means of a probe.

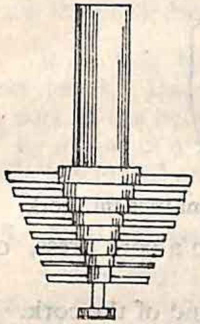


Fig. 1.20. (*a*) A set of cork bores.
(*b*) Selecting a cork borer.

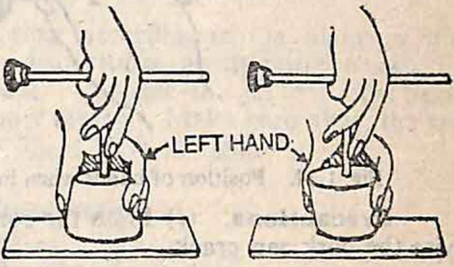


Fig. 1.21. Boring the cork.

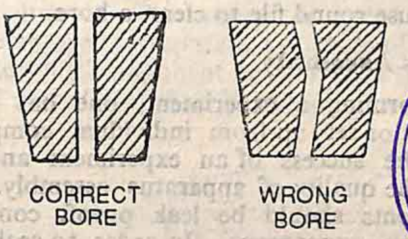


Fig. 1.22. (*a*) A clean straight hole in the cork.
(*b*) Wrong bore.

Now place the cork upside down. Place the bit on the mark and insert it gently till it reaches the end of the cork. Make the bore smooth by removing the bits of cork left inside the hole with the help of glass rod.

(*iv*) Moisten one end of the tube, to be inserted into the cork, with water. The tube and the cork should be held as shown in Fig. 1.23. Now push the tube gently through the hole with a rotatory motion. If the tube is bent, do not hold it at the bend, since the tube

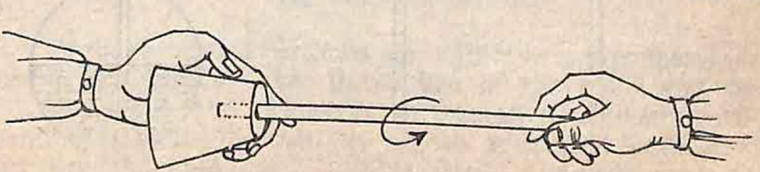


Fig. 1.23. Position of hands when inserting a straight tube into cork

**Solutions of ammonia and sodium hydroxide**

| *Name* | *Molecular formula* | *Approximate normality* | *Preparation* |
|---|---|---|---|
| Conc. ammonia solution | $NH_3$ | 15N | Prepared by diluting the liquefied ammonia. It contains approximately 28% of ammonia by weight. Its specific gravity is ≃0·88. |
| Dilute ammonia solution | $NH_4OH$ | 4N | Dilute 268 ml of the conc. ammonia to one litre by distilled water. |
| Sodium hydroxide solution | NaOH | 4N | Dissolve 176 g sodium hydroxide pellets in distilled water. Cool it and dilute to make the solution one litre. |

### 1.20.6 Preparation of solutions to be used as laboratory reagents.

In the laboratory, reagent solutions of definite concentrations are used. Chamically pure compounds are dissolved in distilled water or some other solvent to prepere their solutions.

If a substance is water soluble, but turbidity or a precipitate appears in its aquous solutions on standing as a result of hydrolysis of the dissolved substance, the appropriate acid is added to the solution (HCl to chlorides, $HNO_3$ to nitrates, and so forth). Some reagents, especially organic ones are not water-soluble, and therefore, organic solvents (alcohol, acetone, and so forth) are used for dissolving thems.

For the preparation of acid and base solutions (laboratory reagents), the procedure has already been suggested. For prepring some other individual reagent solutions, the procedures have been given in appendix.

## ORAL QUESTIONS AND ANSWERS

**Q. 1.1.** Why is a Bunsen burner provided with air holes ?

**Ans.** Gas burns completety in the presence of air and thus the flame becomes non-luminous.

**Q. 1.2.** Which zone of the flame is the hottest ?

**Ans.** The outermost part of the flame, *i.e.*, non-luminous part. Here complete combustion of hydrocarbons take place.

**Q. 1.3.** How are luminous and non-luminous flames obtained ?

**Ans.** When the supply of air is reduced, the flame becomes luminous and smoky. When the air-hole is opened, a non-luminous flame is obtained.

**Q. 1.4.** What type of flame would you use for general heating purposes ?

**Ans.** A non-luminous oxidizing zone of the flame. This part of the flame is surrounded by the oxygen of the air which helps in the complete combustion of hydrocarbons. It is the hottest part of the flame.

**Q. 1.5.** When does the flame jump into the burner ?

**Ans.** This occurs when the proportion of air in the gas-air mixture becomes high.

**Q. 1.6.** What happens when the burner strikes back ?

**Ans.** The burner gets very hot, which may lead to serious consequences such as ignition of the rubber tubing through which the gas is supplied, spoiling of the table, and burning of one's hand.

**Q. 1.7.** How will you control the jumping of the flame into burner ?

**Ans.** By cutting the supply of gas.

**Q. 1.8.** What conditions have to be observed in cutting a glass tube.

**Ans.** 1. Never give multiple scratches with a file.
2. Always give a single jerk while breaking the tube.
3. Hold the tube in both hands in such a way that the thumb nails are on the scratch.

**Q. 1.9.** What happens to the glass tube when the above listed conditions are not followed ?

**Ans.** A smooth cut would not be obtained. Tube with rough and irregular end is obtained.

**Q. 1.10.** While rounding off the freshly cut end of the glass tube, flame, at times, becomes yellow. Comment.

**Ans.** This indicates that the edge melting has begun.

**Q. 1.11.** Why is it not advised to keep the freshly cut end of the glass tube in a flame for a long time while rounding off the edges ?

**Ans.** The tube, if heated for long, gets softened. Finally the open end of the tube gets closed.

**Q. 1.12.** Why is soot deposited on the bent portion of the glass tube not removed while hot ?

**Ans.** Soot being a bad conductor of heat helps in the process of cooling.

**Q. 1.13.** Why is it advisable to blacken the heated part of a tube over a smoking flame after treating it in a non-luminous flame ?

can break and cut your hand. The bent side tube should be held in the left hand and cork should be inserted gently while holding it in the right hand (Fig. 1.24).

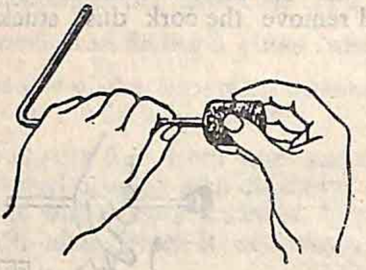


Fig. 1.24. Position of hands when inserting a bent tube into cork

**Precautions**. (*i*) Press the cork gently in a cork press, otherwise the cork can crack.

(*ii*) Keep the borer perpendicular to the end of the cork.

(*iii*) When making two holes on each side of the cork, see that the two holes are straight and parallel.

(*iv*) Do not use round file to clean a bore.

## 1.15 Apparatus Assembly

When performing a experiment, one has to assemble the required apparatus or set up from individual components, generally made of glass. The success of an experiment and also its safety often depend on the quality of apparatus assembly. The apparatus assembled by students should be leak proof, compact and should acquire an attractive appearance. In order to seal the joints of the apparatus where leakage of gas is possible, use wax or plaster of paris. Wax should not be used where heating is required.

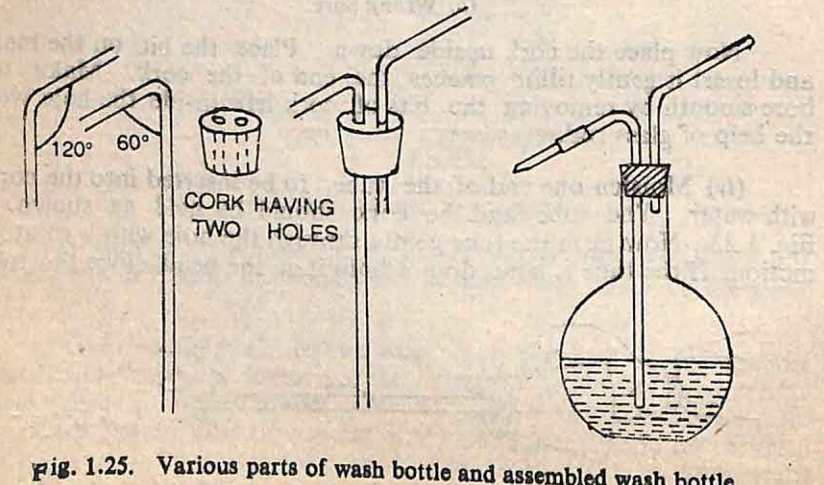


Fig. 1.25. Various parts of wash bottle and assembled wash bottle

For assembling a wash bottle (Fig. 1.25) the following things are required, namely, a flat bottom flask, glass tubing, cork, triangular file, cork borer, rubber tubing, burner and asbestos sheet.

To assemble the apparatus, it is necessary to prepare two glass tubes (one 30 cm long tube bent at an angle of 60° and the other 15 cm long tube bent at an angle of 120°) and a jet.

Bore two holes in a cork according to the diameter of the glass tubes Insert the two bent tubes gently into the cork. Fit the cork in the neck of the flask. Connect the jet to a tube bent at 60° by means of a narrow rubber tubing. Make sure that the wash bottle assembled according to Fig. 1.25 is air tight.

### 1.16. Sedimentation and Decantation

Sedimentation is the process of settling down of heavier particles in a suspension, when it is allowed to stand for some time. This technique of separation is used when the particles in suspension are not fine and therefore settle down easily (Fig. 1.26). The supernatant liquid can thus be easily decanted off (Fig. 1.27) without disturbing the sediment. The process of sedimentation followed by decantation is employed to separate a mixture of a liquid component and an insoluble solid component heavier than the liquid component, *e.g.*, suspended particles of sand in water.

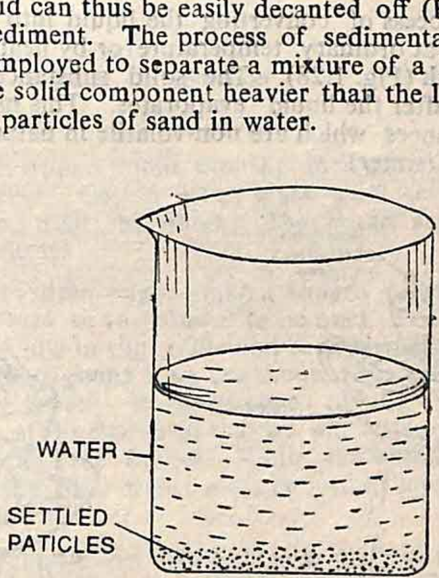


Fig. 1.26. Sedimentation

If the suspended particles are lighter in nature than the liquid, they will get collected over the surface of the liquid and therefore can be scooped out. This type of separation of lighter particles on standing is called *flocculation.* When suspended particles are very fine they take more time in settling down. In such cases, filtration method is employed for separating the particles.

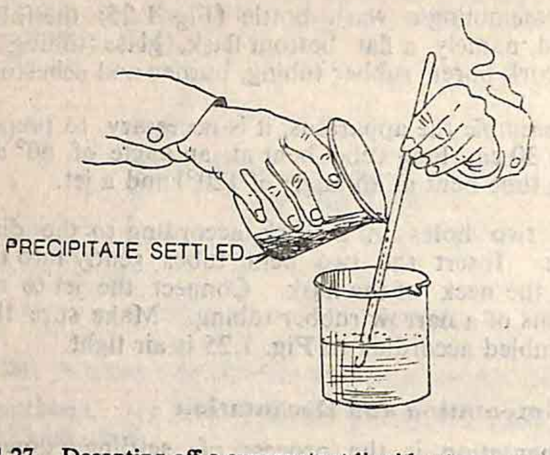


Fig. 1.27. Decanting off a supernatant liquid using a glass rod

## 1.17. Evaporation

It is the process of converting the liquid into vapour either by keeping it in air at ordinary temperature or by heating it on a water bath or sand bath (Fig. 1.28). The solid substance to be purified remains behind after the liquid evaporates. This method is used to purify the substances which are non-volatile in nature and otherwise soluble in liquid (water).

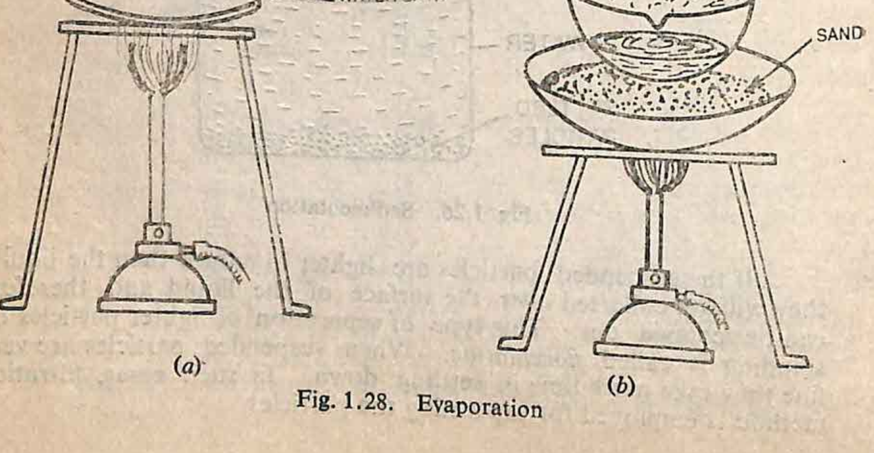
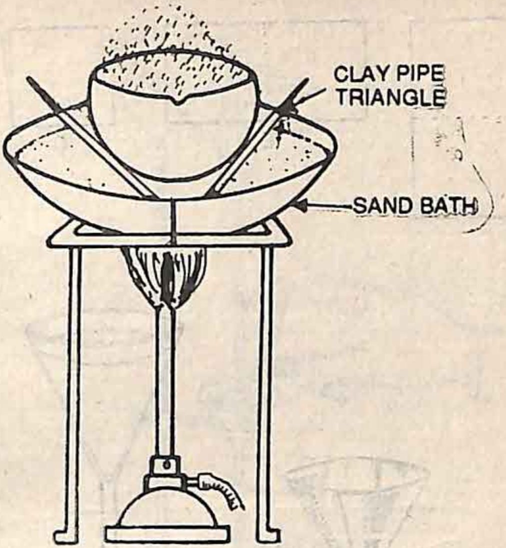

CHINA DISH CONTAINING FILTRATE
WATER BATH
CHINA DISH CONTAINING FILTRATE
SAND
(a)
(b)

Fig. 1.28. Evaporation



(c)

Fig. 1.28. Evaporation

## 1.18. Filtration

To separate solids from a liquid, filtering through paper filters (smooth or fluted) is done. Cotton wool, glass wool or other such materials can also be used as filters. The liquid separated in filtration is called the filtrate.

To make a smooth filter paper, take a square piece of filter paper according to the size of the funnel to be used. Fold it in half as shown by the dashed line in Fig. 1.29*a* and then give another fold. Cut away the outer corners giving it an arc shape. Fix the cone into the funnel with distilled water. Press the edges of the filter paper firmly against the sides of the funnel so that no air bubbles can get between the filter paper and the funnel. While the liquid is being filtered, the edge of the filter paper must be lower than the funnel edge by at least 1·0 cm.

To make a fluted filter paper take a circular piece of filter paper and fold it into quarters. Now open it as shown in Fig. 1.29*b* I. Place 01 along 02 and press the paper, then open it. Put 03 along 02, press and open. The result of these two steps is shown in Fig. 1.29*b* II. Similarly, place 1 along 4, crease and open, then 1 along 5 ; 3 along 5 ; and 3 along 4 (Fig. 1.29*b* III). Next for creating opposite folds, put 01 and 06, crease and hold shut as you place 06 under 04, and so on to make a fan by means of eight opposite folds. Open and you get the fluted filter paper shown in Fig. 1.29*b* IV. With fluted paper, filtration is fast.

**Ans.** Heated part gets covered with soot which works as a bad conductor of heat. Soot covering helps in the process of cooling.

**Q. 1.14.** Why is it advisable to use a broad flame when bending glass tubes ?

**Ans.** To avoid the formation of folds and constrictions at the bend.

**Q. 1.15.** Why is the cork moistened and pressed before boring ?

**Ans.** Cork is made of porous brittle material. Therefore, to avoid cracking of the cork and to get smooth bore, it is moistened with water and pressed in a cork press.

**Q. 1.16.** How should a bent tube be inserted in the hole of the cork ?

**Ans.** When inserting a glass tube in hole of the stopper, moisten the end of the tube. Do not hold it at the bend since the tube can break and cut your hand. The tube should be held as shown in Fig. 1.24.

**Q. 1.17.** Why is it advisable to heat the solution gently while evaporating the solution ?

**Ans.** On strong heating the solution becomes very concentrated and will spit out of the dish as steam is formed beneath semi-solid parts of the mixture.

**Q. 1.18.** What is sedimentation and decantation ?

**Ans.** See section 1.16.

**Q. 1.19.** In what cases, are ordinary filter papers used, and in what cases, are fluted filter papers used ?

**Ans.** When it is desired to retain the precipitate for further operations, ordinary filter paper is used since it is easier to remove the precipitate from such a filter paper. If, on the other hand, the solution only is needed for subsequent operations, a fluted filter paper is used ; filtration in this case proceeds faster owing to a larger filtering area.

**Q. 1.20.** How can you increase the rate of filtration ?

**Ans.** The rate of filtration can be increased by using a suction pump.

**Q. 1.21.** Why is the filter paper made wet with water before starting the filtration ?

**Ans.** Water helps in the proper fixing of the filter paper against the sides of the funnel.

**Q. 1.22.** What is the harm if air gets in between the filter paper and the funnel ?

**Ans.** The rate of filtration will become slow.

**Q. 1.23.** Is water always used to wet the filter paper ?

**Ans.** No, water is not used to wet the filter paper when the liquid to be filtered is not miscible with water.

**Q. 1.24.** How can a liquid be transferred from a beaker to a funnel without spattering, and without running down the outer wall of the beaker ?

**Ans.** By pouring the solution against the stirring rod while the tip of the beaker touches the rod as shown in Fig. 1.30.

□ □

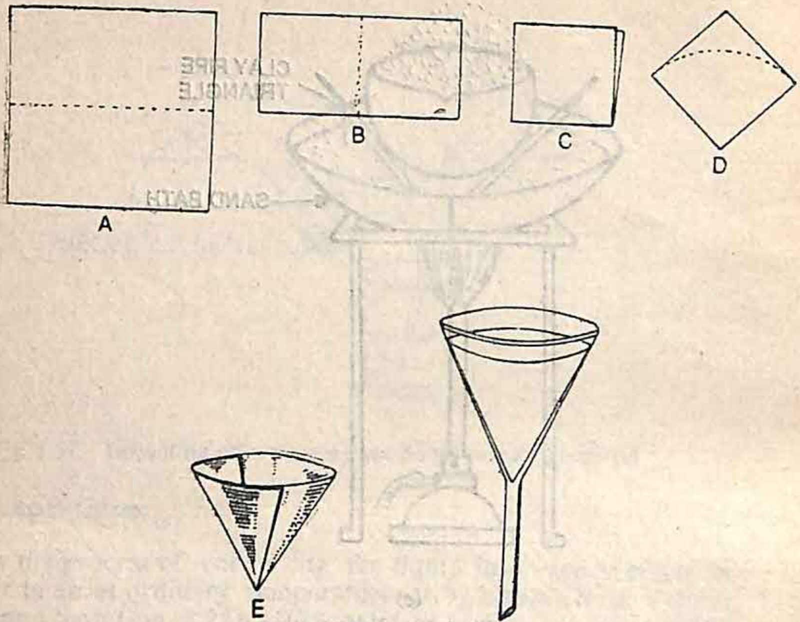


Fig. 1.29 (*a*) Folding of a filter paper.

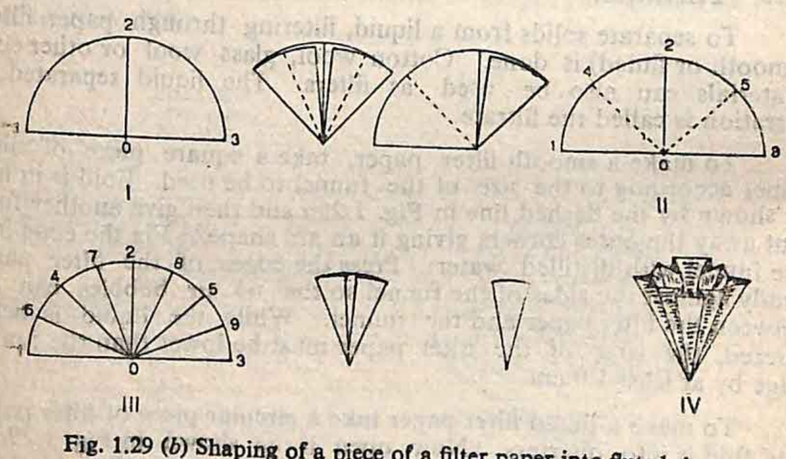


Fig. 1.29 (*b*) Shaping of a piece of a filter paper into fluted shape.

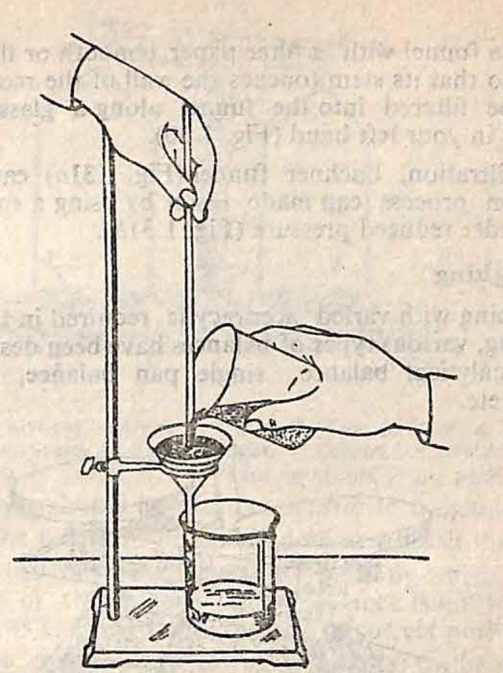


Fig. 1.30. Filtration of a solution.

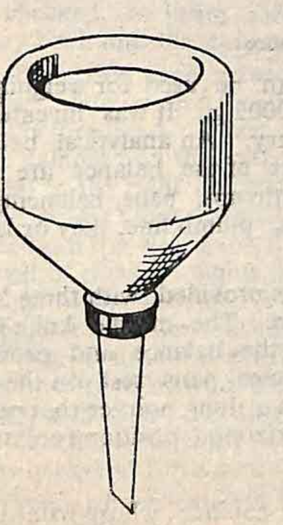


Fig. 1.31 (*a*) Buchner funnel

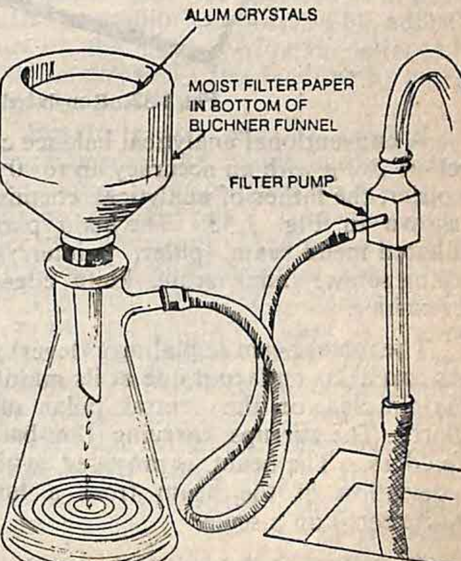


Fig. 1.31 (*b*) Filtration under reduced pressure

Place a funnel with a filter paper (smooth or fluted) in the ring of a stand so that its stem touches the wall of the receiver. Pour the liquid to be filtered into the funnel along a glass rod which you should hold in your left hand (Fig. 1.30).

For filtration, buchner funnel (Fig. 1.31*a*) can also be used. The filtration process can made faster by using a suction pump, *i.e.* filtration under reduced pressure (Fig. 1.31*b*).

## 1.19. Weighing

Weighing with varied accuracy is required in laboratory work. For weighing, various types of balances have been designed : chemical balance, analytical balance, single pan balance, rough balance (Fig. 1.32), etc.

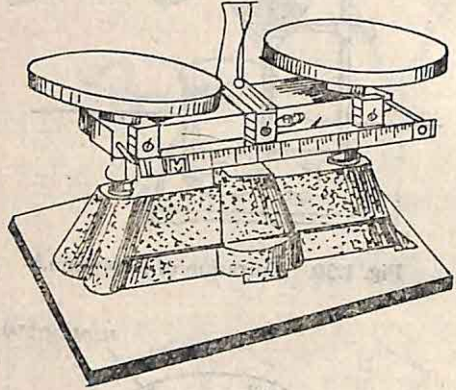


Fig. 1.32. Rough balance

A conventional analytical balance can be used for weighing as much as 200 g with an accuracy up to 0·0002 g. It was invented by Lavoisier, the father of analytical chemistry. An analytical balance is shown in Fig. 1.33. The main parts of the balance are : the graduated metal beam, pillar, pointer, stirrups, pans, balancing or levelling screw, index scale, knife edges, plumb line, key or lever, rider carrier.

The metal beam (equal-arm lever) is provided with three knife edges two at its ends and one at its middle. The middle knife edge rests on a place on the central pillar of the balance and provides support. The stirrups carrying the balance pans rest on the side knife edges. The beam is provided with a long pointer that points the deviation of the beam from a horizontal position (pointer is opposite zero) on a scale.

The balance is housed in a wooden cabinet whose front glass door can to raised and whose side glass doors can be opened. The cabinet protects the balance from dust and air streams. The latter make accurate weighing impossible.

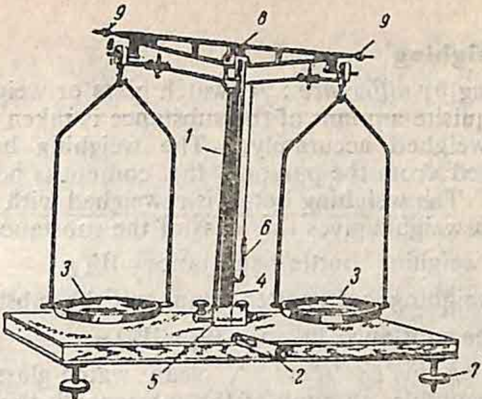


Fig. 1.33. Analytical balance. 1. Pillar, 2. Key, 3. Pans, 4. Pointer, 5. Graduated scale, 6. Plumb weight, 7. Screws for levelling the balance, 8. Beam, 9. Screws for balancing empty pans.

The following should be taken care prior to weighing :

(*i*) Clean the balance with a soft cloth and brush the pans.

(*ii*) Check the balance for accurate levelling which is indicated by the plumbline of the balance. If the balance is not in level, turn the levelling screws to bring the plumbline in correct position.

(*iii*) Gently turn the key (arrester handle) to the right (clockwise) and see the rocking of the pointer.

If the pointer deviates from zero by the same number of divisions to the right and left, consider that the balance is in a good order. If it does not, bring it to the equilibrium position by adjusting the screws provided at the ends of the beam. After the balance has been checked, the beam should be arrested ; this is done by moving the key back into the non-operation position.

**Weighing Operation.** Put the substance to be weighed on a dry glass plate or in a weighing bottle whose weight has been determined before hand. Place the object to be weighed on the left pan of the balance and the weights on the right pan. Turn the handle (or key) to the right and notice the movement of the pointer. If the pointer moves more towards the left, it indicates that the object is lighter than the weights in the right pan. This stage necessitates the removal of certain weights from the pan until the object is counterbalanced by the weights. However, if the pointer moves more towards the right, it indicates that the object is heavier and to counterbalance the object, addition of weights is required. Add or remove weights systematically to or from the right pan until the difference of the weights in the right pan and that of the object is less than 10 mg. Now for final weighing, make use of the rider. When the pointer swings back and forth across the graduated scale an equal number of divisions on each side of the zero mark, the object is considered to show its correct mass. Now arrest the beam and record the weights placed in the right pan and the weight contributed by the rider (as calculated from its position).

**Methods of Weighing**

(*i*) *Weighing by difference* : A watch glass or weighing bottle is weighed. A requisite amount of the substance is taken in a weighing bottle and is weighed accurately. The weighing bottle is then carefully removed from the pan and the content is poured into the beaker or flask. The weighing bottle is reweighed with its remains. The difference in weights gives the mass of the substance taken.

Mass of weighing bottle+substance=$W_1$ g

Mass of weighing bottle after taking out the substance=$W_2$ g

Mass of the substance taken=$(W_1-W_2)$ g

(*ii*) *Weighing by addition* : A clean watch glass is accurately weighed and a suitable amount of the substance is then added to it. Required weights are placed on the right pan. The substance is added or removed from the watch glass a little at a time by a small spatula until the required weights are counterbalanced by the watch glass and its contents. Now when the balance is arrested, the watch glass is removed carefully and the substance is transferred to a beaker (or flask) and the particles of the substance still adhering to the watch glass are washed off with a stream of water from the wash bottle in the beaker. A substance can also be weighed in a weighing bottle but the addition and removal of substance becomes a time-consuming exercise.

Accurate mass of watch glass=$W_1$ g

Mass of watch glass+substance=$W_2$ g

Mass of substance taken=$(W_2-W_1)$ g

*Weight Box*. This is a wooden box with grooves in which the nickel plated metallic weights of mass 50 g, 20 g, 20 g, 10 g, 5 g, 2 g, 2 g, and 1 g are kept (Fig. 1.34). There are fractional weights of

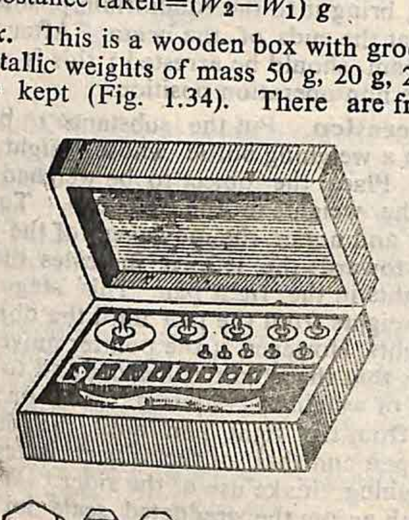


Fig. 1.34. Weight Box.

mass 500 mg, 200 mg, 200 mg, 100 mg, 50 mg, 20 mg, 20 mg, 10 mg, 5 mg, 2 mg, 2 mg, and 1 mg. The fractional weights lower than 10 mg are generally not used. A rider is employed for weights lower than 10 mg.

**Rider**. The rider is a curve shaped small piece of wire. It is made of aluminium, platinum or gold, weighing 10 mg. When the rider is kept in the balance pan or it rests upon the tenth graduation mark of the beam which is vertically above the point of suspension of the pan, its full weight (10 mg) is taken into account. However, its effective weight in milligrams will vary according to the position of the rider on the graduated beam. The beam remains divided into 10 divisions on each side of the centre and the each division is further subdivided in five equal parts indicating 1/5th of a milligram. Divisions are always numbered. The rider on the beam is positioned with a rider carrier which can be moved to and fro. The effective-weight of the rider corresponds to the position in which it is placed.

**Position of rider and its effective weight**

| *Position on division* | *Weight in gram* | *Position on Subdivision* | *Weight in gram* |
|---|---|---|---|
| 1 | 0.001 | 1 | 0.0002 |
| 2 | 0.002 | 2 | 0.0004 |
| 3 | 0.003 | 3 | 0.0006 |
| 5 | 0.005 | 4 | 0.0008 |
| 7 | 0.007 | | |

**Precautions in using the balance**

(*i*) Use the same set of weights and the same balance for all weighings involved in one experiment.

(*ii*) See that the balance is in operational order.

(*iii*) Never place the substances to be weighed directly on the balance pan. Solids are weighed on watch glasses or in weighing bottles whereas volatile, hygroscopic or efflorescent substances and liquids are weighed in stoppered weighing bottles. Caustic alkalis, liquid acids and other corrosive substances should not be weighed in an analytical balance.

(*iv*) Use forceps for lifting the weights. Never touch them with fingers and hands. Weights should never be placed on the table or on the floor of the balance. The weights are kept in a box in a definite order that must be strictly followed when weights are placed in the right pan of the balance.

(*v*) Put weights or loads on the balance pans and remove them only when the pans are arrested and the beam is raised.

(*vi*) Operate the key gently so as not to jerk the balance.

(*vii*) The substance and the weights should be placed on the pans removed from them through the side doors. During weighing, and also when the balance is not being used, all the doors must be shut.

(*viii*) Do not weigh hot objects. Hot crucibles or some other objects, before weighing, be cooled in desiccators to room temperature.

(*ix*) After the weighing, the weights should be replaced in their respective nests in the box with the aid of forceps. The balance and the weights should always be left in order.

(*x*) Record the readings of weighings immediatly in the practical record book.

## 1.20. Preparation of Solutions

The concentration of solutions is, in most cases, expressed by the amount of the solute by weight in a definite weight or volume of the solution or the solvent. More specifically, concentration is usually expressed in one the following ways : as percentage concentration (%), as molar concentration (*M*), as molal concentration (*m*) or as normal concentration (*N*).

### Molar concentrations

The most useful way of expressing exact concentrations of solutions is in terms of moles of solute per litre of solution. Such concentrations are called molar and are designated by the letter '*M*'. It expresses with considerable accuracy the exact number of particles (ions or molecules) per unit of solution volume.

$$\text{Molarity} = \text{moles of solute per litre of solution}$$

$$= \frac{n}{V}$$

where $n$ = number of moles

$V$ = volume in litres of solution

A mole ($6{\cdot}02 \times 10^{23}$ particles) of atoms or molecules is present in the atomic or molecular mass expressed in grams. This mass of any substance that contains a mole of particles is called the molar mass.

Thus, a mole of sodium atoms (atomic mass=23) has mass of 23 g. Therefore, the molar mass of sodium is 23 g $\text{mol}^{-1}$ (g $\text{mol}^{-1}$ means g per mole). Similarly, a mole of water molecules (molecular mass=18) has a mass of 18 g and thus the molar mass of water is 18 g $\text{mol}^{-1}$.

Now the molarity of a solution can be calculated from the expression,

$$\text{Molarity} = \frac{\text{Grams of a solute per litre}}{\text{Grams molecular weight of the solute}}$$

While preparing the dilute solution of desired molarity and volume, we must be careful to distinguish between the concentration (molarity) and the amount (moles) of a solute in a solution. The concentration of a substance in a drop of its solution is the same as its concentration in a litre of the same solution. Obiviously, the amount of the substance in its one litre solution is much greater than it is in the drop. If the drop were diluted to a litre of solution, the moles of solute would remain the same even through the concentration is greatly decreased.

∴ Number of moles before dilution = number of moles after dilution

We know that number of moles = molarity × volume

$$n = M \times V$$

By substituting equals for equals, we get,

$$M_1V_1 = M_2V_2$$

where
$$\frac{\text{mole}}{L} \times L = \frac{\text{mole}}{L} \times L$$

$M_1V_1$ = the number of moles before dilution

$M_2V_2$ = the number of moles after dilution

**Normal Concentration**

The normal concentration of a solution, designated by the letter '$N$' is another way of expressing the concentration of solutions. This method is based on the equivalent mass of the solute. A solution is said to be normal one, when it contains one gram equivalent of the solute per litre of the solution. The equivalent weight expressed in grams is called gram-equivalent. It is important to emphasize here that the gram-equivalent is not invariant as the gram-molecular weight is but depends upon the reaction concerned.

$$\text{Normality} = \frac{\text{Concentration in gram per litre}}{\text{Equivalent weight}}$$

Dilution problems involving normal concentrations are the same as with molar concentrations.

∴ Number of equivalents before dilution

= number of equivalents after dilution

or
$$N_1V_1 = N_2V_2$$

$$\frac{eq}{L} \times L = \frac{eq}{L} \times L$$

As we known that the number of equivalents = $NV$, so it is simply a matter of substituting 'equals for equals'. Accordingly one ml of 1 $N$ solution of any substance will react exactly with 1 ml of 1 $N$ solution of another substance and that solutions of equal normality will react volume for volume.

## Equivalent Mass (or Weight)

The definition of equivalent mass depends upon the type of reaction between the two reactants. The equivalent mass of a substance is that mass which in its reaction can correspond to 8·0 g oxygen or 1 g of hydrogen, or the equivalent. In the context of an acid an equivalent mass (simply called equivalent) of an acid is the mass of an acid that provides one mole of hydrogen ions. Thus, $H_3PO_4$ contains three equivalents per mole, $H_2SO_4$ contains two equivalents per mole and HCl contains one equivalent per mole.

Examples

$$HCl(aq)+NaOH(aq) \longrightarrow NaCl(aq)+HOH(l)$$

$$H_2SO_4(aq)+2NaOH(aq) \longrightarrow Na_2SO_4(aq)+2HOH(l)$$

$$H_3PO_4(aq)+3NaOH\,(aq) \longrightarrow Na_3PO_4(aq)+3HOH(l)$$

Similarly, an equivalent of a base is the mass required to supply one mole of hydroxide ions in a reaction. Thus, in order to find out the equivalent mass, of an acid, it is important to know how many protons of an acid could be replaced by a base. Equivalent mass of an acid is thus defined as that mass of the acid which contains one replaceable hydrogen atom *i.e.*,

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass of acid}}{\text{Number of replaceable H atoms}} = \frac{\text{Molecular mass}}{\text{Basicity}}$$

Similarily, the equivalent mass of a base is the mass of the base which contains one replaceable hydroxyl group, *i.e.*,

$$\text{Equivalent mass of base} = \frac{\text{Molecular mass of base}}{\text{Number of H}^+\text{ ions which react with a molecule of base}} = \frac{\text{Molecular mass}}{\text{Acidity}}$$

The equivalent mass of a salt is generally calculated by dividing the molar mass by the total positive (or negative) valence. Examples of equivalent of some acids, bases, and salts are tabulated below :

**Equivalent masses of some important acids**

| *Name of acid* | *Formula of acid* | *Molecular weight (M) Molar mass (g/mole)* | *Name of replaceable H atoms (B)* | *Equivalent mass (g/equiv.) (M/B)* |
|---|---|---|---|---|
| Hydrochloric acid | HCl | 36.5 | 1 | 36.5 |
| Sulphuric acid | $H_2SO_4$ | 98 | 2 | 49 |
| Nitric acid | $HNO_3$ | 63 | 1 | 63 |
| Oxalic acid | $\begin{array}{l}COOH\\ \vert\\ COOH\end{array} 2H_2O$ | 126 | 2 | 63 |
| Acetic acid | $CH_3COOH$ | 60 | 1 | 60 |
| Phosphoric acid | $H_3PO_4$ | 98 | 3 | 32·7 |

**Equivalent masses of some important bases and salts which behave like bases.**

| *Name of base* | *Formula of base* | *Molcular weight (M) Molar mass (g/mole)* | *Acidity (A)* | *Equivalent mass (g/equiv.) (M/A)* |
|---|---|---|---|---|
| Sodium hydroxide | $NaOH$ | 40 | 1 | 40 |
| Potassium hydroxide | $KOH$ | 56 | 1 | 56 |
| Calcium hydroxide | $Ca(OH)_2$ | 74 | 2 | 37 |
| Sodium carbonate | $Na_2CO_3$ | 106 | 2 | 53 |
| Potassium carbonate | $K_2CO_3$ | 138 | 2 | 69 |
| Sodium bicarbonate | $NaHCO_3$ | 84 | 1 | 84 |
| Potassium bicarbonate | $KHCO_3$ | 100 | 1 | 100 |

**Equivalent masses of some important salts**

| *Compound* | *Molar mass (g/mole)* | *Total positive volume* | *Equivalent mass (g/equiv.)* |
|---|---|---|---|
| $KCl$ | 74·5 | 1 | 74·5÷1=74·5 |
| $NaCl$ | 58·5 | 1 | 58·5÷1=58·5 |
| $Na_2SO_4$ | 142 | 2 | 142÷2=71 |
| $AlCl_3$ | 133·5 | 3 | 133·5÷3=44·5 |
| $Al_2(SO_4)_3$ | 342 | 6 | 342÷6=57 |

The equivalent weight of a substance involved in oxidation-reduction titrations is defined as the weight of the substance which consumes or produces 1 mole of electrons directly or indirectly. Numerically, this may be expressed as follows :

$$\text{Equivalent weight}=\frac{\text{Molecular (or ionic) weight}}{\text{Number of electrons gained or lost per molecule (or ion) of the substance}}$$

From the above definition it follows that the determination of the equivalent weight of an oxidizing or reducing agent involves the following steps :

(*i*) Complete and balanced ionic equation for its reduction or oxidation reaction, and

(*ii*) The number of electrons required or lost per molecule as per the balanced ionic equation. The balanced ionic equation of $KMnO_4$ in acid solution is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

From this equation it is evident that five electrons are gained by each $MnO_4^-$ during the course of the reaction.

Therefore,

$$\text{Equivalent weight of } MnO_4^- = \frac{\text{Ionic weight of } MnO_4^- \text{ ion}}{5}$$

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight of } KMnO_4}{5}$$

$$=\frac{158}{5}=31.6$$

The following table gives the equivalent weights of commonly used substances in redox titrations.

| *Name of the substance* | *Molecular formula* | *Molecular weight* | *Ion-electron equation* | *Number of electrons gained or lost per molecule (n)* | *Equivalent weight (M/n)* |
|---|---|---|---|---|---|
| Potassium permanganate | $KMnO_4$ | 158 | $MnO_4^- + 8H^+ + 5e^-$<br>$\rightarrow Mn^{2+} + 4H_2O$ | 5 | $\frac{158}{5} = 31.6$ |
| Ferrous sulphate | $FeSO_4.7H_2O$ | 278 | $Fe^+ \rightarrow Fe^{3+} + 1e^-$ | 1 | $\frac{278}{1} = 278$ |
| Mohr's salt | $FeSO_4.(NH_4)_2SO_4.6H_2O$ | 392 | $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$ | 1 | $\frac{392}{1} = 392$ |
| Oxalic acid | $\begin{array}{c} COOH \\ \vert \\ COOH \end{array} 2H_2O$ | 126 | $\begin{array}{c} COO^- \\ \vert \\ COO^- \end{array} \rightarrow 2CO_2 + 2e^-$ | 2 | $\frac{126}{2} = 63$ |
| Potassium dichromate | $K_2Cr_2O_7$ | 294 | $Cr_2O_7^{2-} + 14H^+ + 6e^-$<br>$\rightarrow 2Cr^{3+} + 7H_2O$ | 6 | $\frac{294}{6} = 49$ |

## Standard Solutions

A solution of known concentration is considered as a standard solution. The strength of a standard solution is expressed in gram equivalents per litre or moles per litre. For example, if 8 g of a substance is dissolved in one litre solution, its strength is 8 g/*L*.

Some of the standard solutions are prepared by weighing out accurately and dissolving the weighed solute in a suitable solvent and making up the solution to a known volume. Standard solutions of sodium carbonate, oxalic acid, potassium dichromate, etc. are prepared in this way. These substances are available in the pure form (analytical grade) and are called primary standard substances. Their solutions of known concentration are called primary standard solutions as other solutions are standardized against them.

A primary standard substance must have the following characteristics :

(*i*) It should be easily available in the pure state.

(*ii*) It should be stable at room termperature.

(*iii*) Its composition should not change when stored.

(*iv*) It should be readily soluble in water.

Crystalline oxalic acid, sodium carbonate and Mohr's salt, etc., have all the characteristics of primary standard substances.

Substances which do not meet the above requirements are called secondary standard substances. Standard solutions of these substances cannot be prepared by dissolving their known amount in a solvent. For the preparation of standard solutions of such substances, as HCl, $H_2SO_4$, $KMnO_4$, NaOH a aqueous ammonia, etc., first solutions of approximate concentration are prepared and are then standardized by titrating against a suitable primary standard solution. Concentrated HCl is about 12 *N* and the strength of conc. $H_2SO_4$ is about 36 *N*. Hence, the solutions of these acids of approximate strength are prepared by diluting their calculated volume to a known volume.

### 1.20.1. Preparation of the standard solution

(1) Take a clean and dry weighing bottle. Weigh the weighing bottle accurately and record its weight in your record book.

(*ii*) Put the substance with a spatula in the weighing bottle and take its weight again. The difference between the initial weight of the weighing bottle and that of weighing bottle with its contents should correspond to the calculated amount of the substance. Again record its weight in your record book.

(*iii*) Transfer the weighed substance from the weighing bottle to a 250 ml beaker (Fig. 1.35). If the substance is weighed by difference method, the weighing bottle should now be weighed again. If not, the weighing bottle should be washed with its contents. Transfer these washings to the beaker.

(*iv*) Add distilled water from a wash bottle along the sides of the beaker so that there is no splashing.

(*v*) Dissolve the substance by stirring it gently with a glass rod.

(*vi*) After ensuring the complete dissolution of the substance transfer the entire solution into a measuring flask with the help of a funnel [Fig. 1.36(*a*)].

(*vii*) Wash the entire interior surface of the beaker with distilled water and transfer the washings into the measuring flask [Fig. 1.36(*b*)].

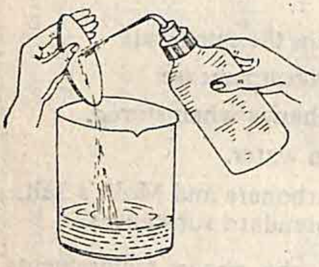


**Fig. 1.35. Transferring of a weighed substance to a beaker for dissolution.**

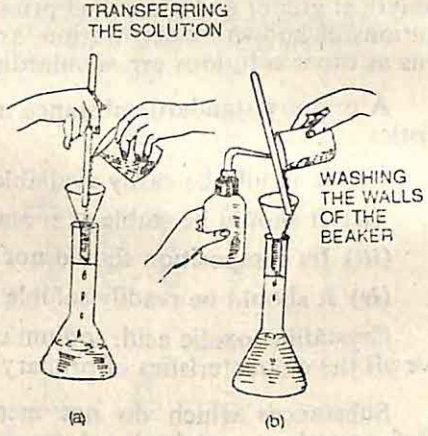


**Fig. 1.36. (*a*) Transferring the solution into a measuring flask, (*b*) Washing the inner surface of the beaker and transferring the washings into the flask.**

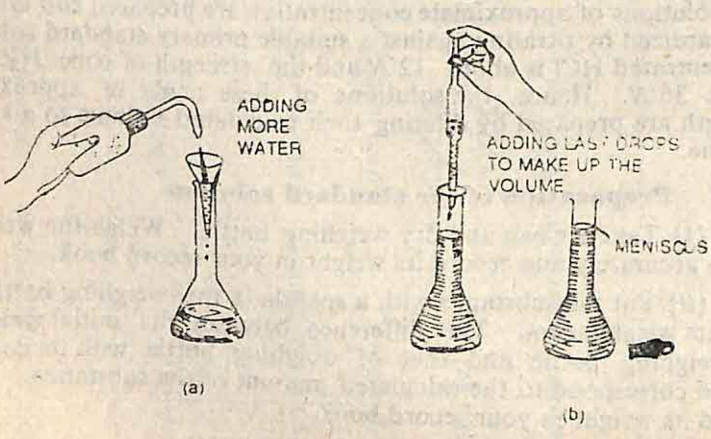


**Fig. 1.37. (*a*) Addition of water, (*b*), (*c*) Addition of last drops of water to make up the volume.**

(*viii*) Now add more of distilled water from a wash bottle taking care not to fill upto the mark but a little below it [Fig. 1.37(*a*)]. Finally add a few drops of distilled water with a pipette until the lower level of the meniscus just coincides the graduated mark on the flask [Fig. 1.37(*b*), (*c*)].

(*ix*) The measuring flask is then stoppered and shaken vigorously for a few minutes to make the solution homogeneous.

**Note** : 1. The substance can be weighed in a watch glass also.

2. The weighed substance can be transferred directly into a measuring flask to avoid the loss of a substance. Any spoilage invalidates the result.

### 1.20.2. Preparation of a standard solution of oxalic acid

Molecular formula of oxalic acid $=(COOH)_2.2H_2O$

Molecular weight of oxalic acid $=126$ g.

To prepare 1000 ml of 1M oxalic acid, 126 g of oxalic acid is required. To prepare 1000 ml of $\frac{M}{10}$ oxalic acid $\frac{126}{10}$ g or 12·6 g of oxalic acid is required. And to prepare 250 ml of $\frac{M}{10}$ oxalic acid $\frac{12\cdot6\times250}{1000}$ g or 3·15 g of oxalic acid is required.

Now to prepare a normal solution, equivalent weight of oxalic acid is required. Its equivalent weight is half of its molecular weight as the oxidation of one molecule of oxalic acid liberates two electrons or it contains two replaceable hydrogen atoms. Now to prepare 250 ml of $\frac{N}{10}$ oxalic acid, $\frac{63\times250}{1000}$ g or 1·575 g of oxalic is required.

In general,

$$\text{Normality}=\frac{\text{Mass of substance}}{\text{Equivalent weight}}\times\frac{1000}{\text{Volume of solution}}$$

$$\text{Normality}=\frac{1}{10}$$

Mass of substance required $=x$ g

Equivalent weight $=63$

Volume of solution required $=250$ ml

$$\frac{1}{10}=\frac{x}{63}\times\frac{1000}{250}$$

$$x=\frac{1}{10}\times\frac{63\times250}{1000}=1\cdot575 \text{ g}$$

Now weight the calculated amount of oxalic acid as suggested in sections 1·19 and 1.20.1. Dissolve the sample as suggested.

$$\text{Weight of watch glass} = w_1 \text{ g}$$

$$\text{Weight of watch glass} + \text{oxalic acid} = w_2 \text{ g}$$

$$\text{Weight of oxalic acid} = (w_2 - w_1) \text{ g}$$

$$\text{Volume of solution prepared} = 250 \text{ ml}$$

$$\text{Normality of oxalic acid} = \frac{w_2 - w_1}{63} \times \frac{1000}{250} = \frac{4\,(w_2 - w_1)}{63}$$

$$\text{Molarity of oxalic acid} = \frac{w_2 - w_1}{126} \times \frac{1000}{250} = \frac{4\,(w_2 - w_1)}{126}$$

The terms 'mass' and 'weight' are loosely equated in practice.

### 1.20.3. Preparation of a standard solution of sodium carbonate

The molecular formula of anhydrous sodium carbonate is $Na_2CO_3$.

The equivalent weight of a salt taking part in an acid-alkali titration is calculated by making use of the law of equivalents or using the formula,

$$\text{Equivalent weight of } Na_2CO_3 = \frac{\text{Molecular weight}}{\text{Acidity}}$$

$$= \frac{106}{2} = 53$$

Thus to prepare 1000 ml of 1 N sodium carbonate solution 53 g of salt are required.

To prepare 1000 ml of *N*/10 sodium carbonate solution, 53/10 g or to prepare 250 ml of *N*/10 sodium carbonate solution $\frac{53 \times 250}{1000}$ g or 1·325 g of sodium carbonate are required.

Weigh 1·325 g of sodium carbonate in a watch glass and dissolve the sample as suggested in section 1.20.1.

$$\text{Weight of watch glass} = w_1 \text{ g}$$

$$\text{Weight of watch glass} + \text{sodium carbonate} = w_2 \text{ g}$$

$$\text{Weight of sodium carbonate} = (w_2 - w_1) \text{ g}$$

$$\text{Volume of solution prepared} = 250 \text{ ml}$$

Normality of sodium carbonate

$$= \frac{\text{Mass of sodium carbonate}}{\text{Equivalent weight}} \times \frac{100}{\text{Volume of solution}}$$

$$= \frac{(w_2 - w_1)}{53} \times \frac{1000}{250}$$

$$\text{Normality}=\frac{4(w_2-w_1)}{53}$$

Molecular weight of sodium carbonate = 106

$$\text{Molarity of sodium carbonate}=\frac{4\,(w_2-w_1)}{106}$$

### 1.20.4. Standard solutions of acids

The most commonly used acid solutions in the laboratory are hydrochloric, sulphuric, nitric and acetic acids. These acids cannot be weighed like crystalline substances for preparing their solutions of known concentrations. Therefore, it is important to know the methods by which their standard solutions can be prepared. The concentrations of these commonly used acids are as follows :

| *Acid* | *Specific gravity* | *Approximate normality* |
|---|---|---|
| Hydrochloric acid | 1·19 | 12 N |
| Nitric acid | 1·42 | 16 N |
| Sulphuric acid | 1·84 | 36 N |
| Acetic acid | 1·05 | 14 N |

For preparing dilute solutions of acids of required concentrations of acids, we can use the normality equation to calculate the volume of a given acid to be taken.

$$N_1V_1=N_2V_2$$

For example, if we have to prepare 250 ml of 5N sulphuric acid from 36 N concentrated acid, the volume of concentrated sulphuric acid required will be about 35, *i.e.*,

$$36\text{ N}\times V_1=5\text{N}\times 250$$

$$\text{or}\qquad V_1=\frac{5\times 250}{36}=\frac{1250\text{ ml}}{36}\cong 35\text{ ml}$$

Thus, 35 ml of concentrated sulphuric acid is taken and diluted to 250 ml in a measuring flask. **The acid should be poured into water and not water into the acid**. This acid solution will be about 5N because the acid available in the market may not be exactly 36 N.

For preparing 250 ml of $N/10$ sulphuric acid, the concentrated acid required will be about 0 7 ml, *i.e.*,

$$36\text{ N}\times V_1=\frac{N}{10}\times 250$$

$$\text{or}\qquad V_1=\frac{25}{36}\cong 0{\cdot}7\text{ ml}$$

### 1.20.5. Preparation of dilute solutions (known concentrations) of sulphuric acid

(*i*) To prepare 250 ml N $H_2SO_4$ take 7 ml pure conc. $H_2SO_4$ with the help of a measuring cylinder (10 ml capacity) and pour it slowly into the 500 ml beaker containing about 200 ml distilled water. Stir the solution by a glass rod. After all the acid has been added allow the solution to stand at room temperature. Now transfer the solution into a 250 ml measuring flask with the help of a funnel. Add more of distilled water upto the mark. After stoppering the measuring flask, shake the solution thoroughly for 2-3 min to make the solution homogeneous. The solution will be about 1N.

The solution of $H_2SO_4$ can be standardized by titrating against standard sodium carbonate solution. The detailed procedure for standardizing the solution is given in unit 9.

(*ii*) To prepare 250 ml 0·1 N $H_2SO_4$ 0·7 ml pure conc. $H_2SO_4$ witd the help of a measuring cylinder (1·0 ml or 10 ml capacity). Now follow the procedure as given above. Label the resulting solution as *N*/10 $H_2SO_4$.

**Remarks.** (*i*) When ~22·5 ml of conc. hydrochloric acid is added to 222·5 ml of distilled water the dilute solution so prepared would approximately be of strength 1 N (or 1 M).

(*ii*) When ~ 16 ml of conc. nitric acid is added to 234 ml of distilled water, the dilute solution of the acid so prepared would approximately be of strength 1 N (or 1 M).

(*iii*) When ~ 7·0 ml of conc. $H_2SO_4$ is added to 243 ml of distilled water, the dilute solution of the acid so prepared would approximately be of strength 1N (or 0·5 M because basicity of $H_2SO_4$ is 2).

**Precautions.** 1. Acids being highly corosive, should be handled with extreme care.

2. Aprons should be used to protect clothes.

3. While preparing dilute solutions of acids, acids should be added into water. Special care should be taken in the case of sulphuric acid.

The following tables include the details about the common concentrated acids and outlines for preparing dilute acids from them.

**Concentrated acids**

| *Acid* | *Percent by weight* | *Approximate specific gravity* | *Normality* | *Volume required to make 1 litre of approximately 1 N solution (ml)* | *Volume required to make 250 ml of approximately N/10 solution (ml)* |
|---|---|---|---|---|---|
| Hydrochloric acid (HCl) | 35 | 1·18 | 12 N | 90 | 2·2 |
| Nitric acid ($HNO_3$) | 70 | 1·42 | 16 N | 65 | 1·6 |
| Sulphuric acid ($H_2SO_4$) | 98 | 1·84 | 36 N | 30 | 0·7 |
| Acetic acid ($CH_3COOH$) | 99·6 | 1·05 | 16 N | 60 | 1·5 |

## Diluted acids

| *Acid* | *Approximate normality* | *Preparation* |
|---|---|---|
| Hydrochloric acid (HCl) | 4 N | Dilute 334 ml of conc. HCl to 1 litre with distilled water. |
| Nitric acid ($HNO_3$) | 4 N | Dilute 248 ml of conc. $HNO_3$ to 1 litre with distilled water |
| Sulphuric acid ($H_2SO_4$) | 4 N<br>(2 M) | Add 112 ml of conc. $H_2SO_4$ slowly and with constant stirring into about 500 ml of distilled water. Cool it and make upto 1 litre by distilled water. |
| Acetic acid ($CH_3COOH$) | 4 N | Dilute 255 ml of glacial acetic acid to 1 litre with distilled water |

NOTE : For diluting sulphuric acid solutions, the acid is added into water. Water is never added to the sulphuric acid solution.

### 1.20.5. Preparation of dilute solutions (known concentrations) of bases.

The most commonly used base solutions in the laboratory are sodium hydroxide and aqueous ammonia. Sodium hydroxide is a deliquescent solid ; its standard solutions cannot therefore be prepared by direct weighing. It is usual to prepare a solution of approximately the concentration required and then to standardize it against standard oxalic acid solution (unit 9).

Ammonium hydroxide in solution is only slightly split up into ammonium and hydroxide ions. Because of this, at times, it is called aqueous ammonia. On standing, dissolved ammonia gas evaporoates. Its strength decreases with lapse of time. It is usual to prepare its standard solution as and when required. A solution of ammonium hydroxide smells of ammonia. This is because the reaction of ammonia with water is revessible.

$$NH_4OH(aq) \rightleftharpoons NH_3\,(g) + H_2O(l)$$

The decomposition is accelerated by heat and also by blowing air through the solution.

The following table includes the details about the solutions of ammonia and sodium hydroxide and their method of preparation.

# UNIT 2

## Purification of Soluble Salts and Preparation of Crystals

### 2.1. Introduction

A substance used in chemistry should be pure. If not, we get wrong ideas about it. In daily life, 'pure' has a different meaning. We buy pure honey. We eat pure butter. We wear clothes made of pure wool. Honey, butter and wool are mixtures. In science then 'pure' has only one meaning. A pure substance is a single substance. Definite physical and chemical properties and colour and shape of the crystals of a substance are attributed to its purity. The nature of the substance to be purified determines the method of purification to be used. The most widespread technique is re-crystallization for soluble solids.

Chemical substances can be recognized by the shape of their crystals and their colours. A substance (element or compound) acquires a definite crystalline shape depending on the conditions under which it crystallizes out from its solution. Growing crystals provide a pleasing experience and wonderful sight to chemists. The crystals, if grown under suitable conditions, will appear in their desired form. However, some crystals are easier to grow than others, *e.g.*, large crystals of common salt and washing soda are difficult to obtain while those of alums are easier to grow.

### 2.2. Formation of Crystals

One should bear in mind the following points while growing crystals from their solutions :

(*i*) Crystals can only be obtained from a saturated solution of a substance because a cold solvent is unable to hold as much solute as a hot solvent.

(*ii*) Inorganic substances are more soluble in hot water.

(*iii*) For the proper growth of crystals, at times, a bit of crystal called 'nucleus' is required, around which the crystal can grow. It may also result from the molecules present in solution coming closer by chance. More often it is provided by some particle of dust, caught by the solution as per chance only. A dirty solution can provide a larger number of nuclei, thus resulting into the growth of many small crystals. Therefore, the solution should always be filtered and protected from dust particles before keeping for crystallization.

(*iv*) Evaporation or quick cooling of hot saturated solution should be avoided. As a result, the excess solute is deposited from the solution, and the deposit is obtained as crystals. Thus rapid cooling will give small crystals.

Slow cooling of the hot saturated solution (gradual crystallization) will give fewer but large crystals.

(*v*) During the course of crystallization, the solution should not be disturbed. The size and shape of crystals may change on disturbing the solution.

The process of crystal formation involves the following steps :

1. **Preparation of saturated solution of a substance.** A saturated solution is defined as one that contains the maximum amount of solute at a given temperature. Thus, a saturated solution is prepared by taking a required amount of the substance in a beaker and adding water just sufficient to dissolve the substance. At times, a saturation stage is reached by concentrating the solution.

2. **Filtration.** The saturated solution is filtered hot in a china dish to remove any suspending impurities.

3. **Crystallization**. The filtrate of hot saturated solution is cooled slowly to initiate the process of gradual crystallization.

4. **Filtration and drying of crystals.** When the process of crystallization is complete, the solution left is decanted off. The decanted solution is still saturated and is called the "mother liquor". At times, filtration is also required. The crystals are then washed with ice-cold water to remove the adhering mother liquor. They are then dried by spreading over a layer filter paper.

## 2.3. Experiments

**Experiment 2.1**. To obtain pure common salt crystals from common salt (commercial).

Or

To purify common salt (commercial) by crystallization.

**Apparatus** Beakers, funnel, glass rod, filter paper, evaporating dish, funnel stand, tripod stand, wire guaze, burner, mortar and pestle.

**Chemicals**. Commercial sample of common salt.

**Procedure.** (*i*) Grind some commercial sample of common salt with a pestle in mortar and weigh out roughly 10 g. Add the salt in lots to about 50 ml of distilled water until, even with vigorous shaking, no more of it dissolves. To this cold saturated solution add a few more grams of salt and warm the solution with stirring. The salt will dissolve, leaving the impurities in suspension. Filter the hot solution into a evaporating dish. When the warm solution cools, the extra quantity of salt added will crystallize out. This does not give good yield.

(*ii*) For a better yield, heat the solution gently on a sand bath and concentrate it to a saturation point (Fig. 2.1). To test the stage of saturation point, blow air from mouth on a glass rod dipped into solution (Fig. 2.2). If a white deposit appears immediately on the glass rod, the solution is saturated.

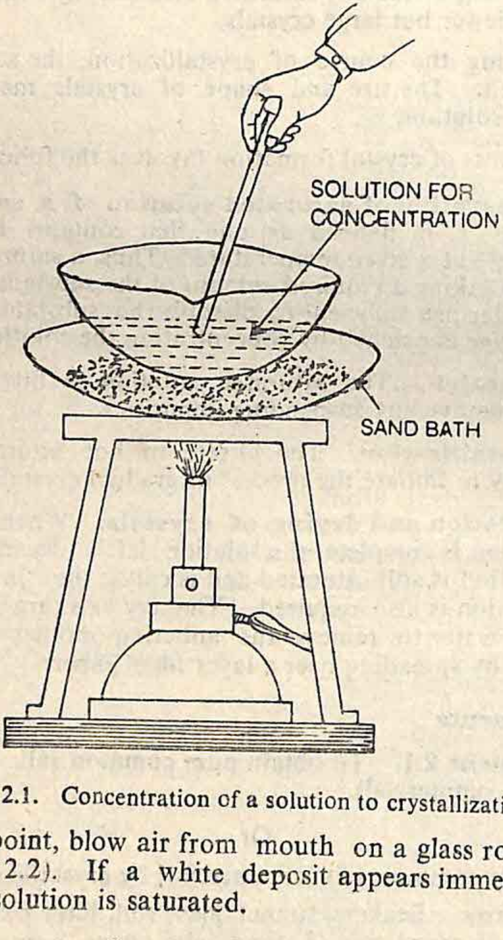


Fig. 2.1. Concentration of a solution to crystallization.

After the saturation stage is reached, stop heating the solution and allow the solution to cool undisturbed.

(*iii*) Crystals of the salt will appear after some time. When the contents of the dish are sufficiently cold and the crystallization of the salt is complete decant off the mother liquor (Fig. 2.3).

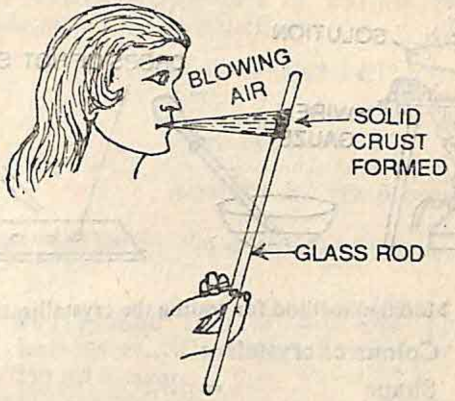


Fig. 2.2. Testing the crystallization point.

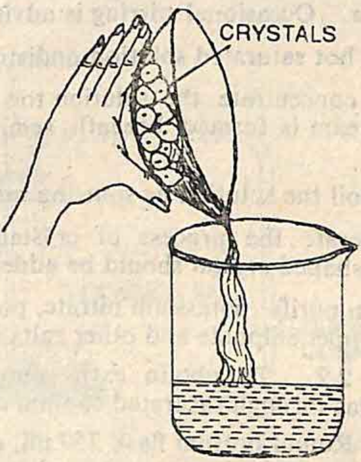


Fig. 2.3. Decanting off the mother liquor from the crystals.

(*v*) Wash the crystals in the dish with ice-cold water to remove the adhering mother liquor. Dry the crystals by spreading them over a fold of filter papers (Fig. 2.7). Crystals will have the definite shape, like cubes.

**Note.** The attainment of saturation point can be tested by a modified method as follows :

Take up some of the hot liquid in a dropper. Put drops on a glass slide (Fig. 2.4). White bits should form immediately in the drops.

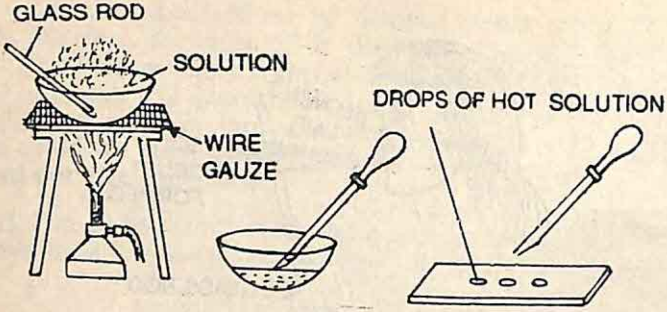


Fig. 2.4. Modified method for testing the crystallization point.

**Results.** Colour of crystals= ......
Shape = ......
Yield = ......
Percentage yield = ......

**Precautions**. (*i*) Gentle heating should be done to ensure uniform evaporation. Occasional stirring is advised.

(*ii*) Cool the hot saturated solution undisturbed.

(*iii*) Do not concentrate the solution too much, as it will spit out of the dish as steam is formed beneath semi-solid parts of the mixture.

(*iv*) Do not boil the solution as spurting may occur.

(*v*) To accelerate the process of crystallization and to get a large crystal a well shaped crystal should be added.

**Note**. One can purify potassium nitrate, potassium and sodium sulphates, alums, copper sulphate and other salts in this way.

**Experiment 2.2**. To obtain extra pure salt by passing hydrogen chloride gas through saturated sodium chloride solution.

**Apparatus**. Round bottom flask 250 ml, cork with two holes, thistle funnel, delivery tube, wire guaze, tripod stand, beaker, funnels, burner, iron stand and clamp.

**Chemicals**. Impure salt and conc. sulphuric acid

**Principle**. Commercial salt remains mixed with impurities such as calcium sulphate and magnesium sulphate. Pure sodium chloride in the form of white small granuels can be obtained by passing hydrogen chloride gas through a saturated solution of common salt. Hydrogen chloride gas is soluble in water and it furnishes $H^+$ and $Cl^-$ ions, thus increasing the concentration of $Cl^-$ ions in the solution. Due to the increase in concentration of the common $Cl^-$ ion, sodium chloride will precipitate out in extra pure form leaving behind the impurities in the solution. From the process it can be inferred that the purification of sodium chloride is based upon the principle of 'common ion effect'.

$$\underset{\text{(Solution)}}{\text{NaCl}} \longrightarrow \text{Na}^+ + \text{Cl}^-$$

$$\text{Na}^+ + \text{Cl}^- \xrightarrow[\text{from HCl gas}]{\text{Excess of Cl}^-} \underset{\text{(Extra pure)}}{\text{NaCl}\downarrow(s)}$$

**Procedure**. (*i*) Set up the apparatus for producing hydrogen chloride gas.

(*ii*) Take well ground 10 g of salt and prepare saturated solution of it in hot water. Cool the solution to room temperature and filter into a 250 ml beaker.

(*iii*) Pass hydrogen chloride gas through the solution using the funnel arrangement as shown in Fig. 2.5. Pure sodium chloride will separate out as white granules. Continue to pass the gas until no more of the salt precipitates out.

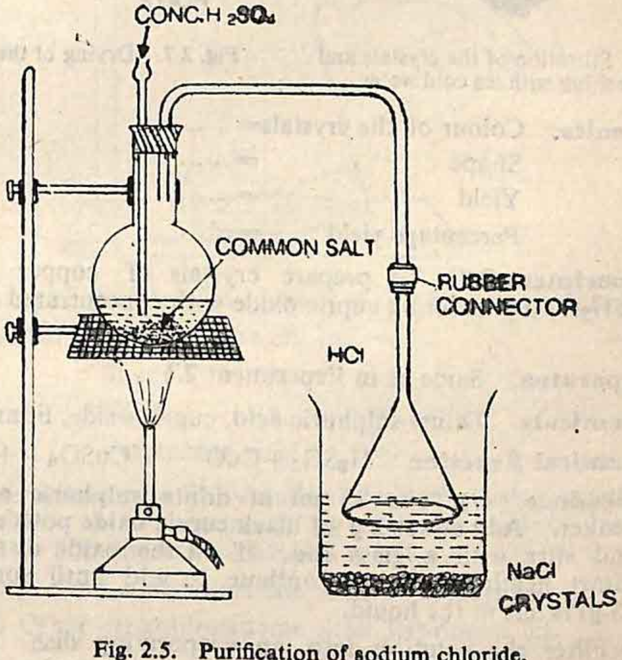


Fig. 2.5. Purification of sodium chloride.

(*iv*) Filter the white granuels through a filter paper (for folding of filter paper refer to unit 1 section 1.18) fixed in a funnel (Fig. 2.6) Wash the crystals with a small amount of ice cold water. Dry the crystals by spreading them over a fold of filter papers (Fig. 2.7).

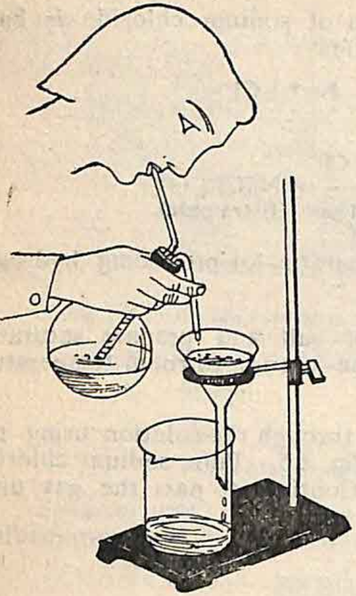


Fig. 2.6. Filtration of the crystals and their washing with ice cold water.

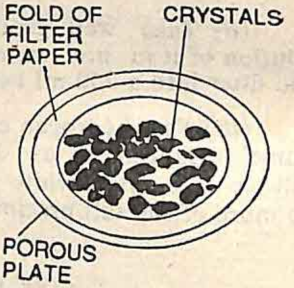


Fig. 2.7. Drying of the crystals.

**Results.** Colour of the crystals= ......
Shape = ......
Yield = ......
Percentage yield = ......

**Experiment 2.3.** To prepare crystals of copper sulphate ($CuSO_4.5H_2O$) by reacting cupric oxide with concentrated sulphuric acid.

**Apparatus.** Same as in Experiment 2.1.

**Chemicals.** Dilute sulphuric acid, cupric oxide, litmus paper.

**Chemical Reaction.** $H_2SO_4 + CuO \longrightarrow CuSO_4\downarrow + H_2O$

**Procedure.** (*i*) Take 25 ml of dilute sulphuric acid in a 250 ml beaker. Add about 2 g of black cupric oxide powder. Heat gently and stirr with a glass rod. If all the oxide dissolve, add more. Start heating again. Continue to add until some oxide (total ~5 g) is left in the liquid.

(*ii*) Filter the solution into an evaporating dish. Heat the solution gently on a sand bath and concentrate it to the saturation point (test the saturation point as described in Experiment 2 1).

(*iii*) Stop heating the solution and allow the solution to stand for crystallization.

(*iv*) After an interval of time, blue coloured crystals will appear. Decant off the mother liquor and wash the crystals with ice cold water to wash off the mother liquor adhering to the crystals. Dry the crystals by spreading them over a fold of filter papers (Fig. 2.7).

By making use of the apparatus called vacuum filter (Fig. 2.8). crystals can be dried fast without any loss.

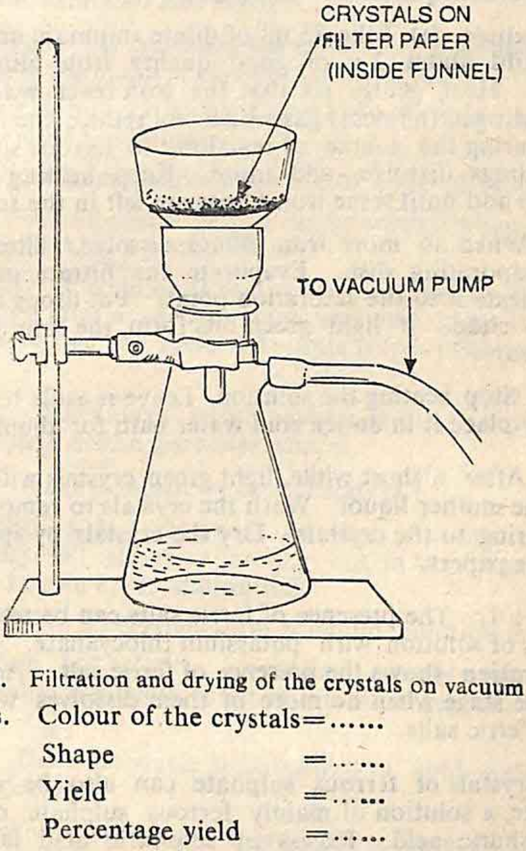


Fig. 2.8. Filtration and drying of the crystals on vacuum filter.

**Results.** Colour of the crystals= ......

Shape = ......

Yield = ......

Percentage yield = ......

**Precautions.** (*i*) The solution to be evaporated should be acid free. This is to be ascertained by a litmus paper. Undissolved cupric oxide also shows that no acid is left.

(*ii*) Do not concentrate the solution to dryness.

(*iii*) Other precautions same as in Expriment 2.1.

**Note.** One can purify the impure sample of copper sulphate by preparing a saturated solution of prepared impure sample of copper sulphate and then concentrating it to a saturation point as suggested in experiment 2.1. The other details are given under experiment 2.3.

**Experiment 2.4.** To prepare crystals of ferrous sulphate ($FeSO_4.7H_2O$) by reacting iron filings with dilute sulphuric acid.

**Apparatus.** Same as in Experiment 2.1.

**Chemicals.** Iron filings, dilute sulphuric acid, potassium thiocyanate solution, litmus paper.

**Chemical Equation.** $Fe+H_2SO_4 \longrightarrow FeSO_4\downarrow+2H$

**Procedure.** (*i*) Take 25 ml of dilute sulphuric acid in a 250 ml beaker. Add about 2 g of good quality iron filings (total iron filings 5 g). Heat gently so that the iron reacts with the acid and liberates hydrogen (nascent) gas which will reduce the ferric sulphate, if formed during the course of reaction, to ferrous sulphate. If all the iron filings dissolve, add more. Keep heating the contents. Continue to add until some iron filings are left in the solution.

(*ii*) When no more iron filings dissolve, filter the solution into an evaporating dish. Evaporate the filtrate on a sand both and concentrate it to the saturation point. Put drops of hot solution on a glass slide. If light green bits form, the saturation point has been reached.

(*iii*) Stop heating the solution. Leave it aside to form crystals. If necessary place it in an ice cold water bath for about half an hour.

(*iv*) After a short while, light green crystals will appear. Decant off the mother liquor. Wash the crystals to remove any mother liquor adhering to the crystals. Dry the crystals by spreading over a fold of filter papers.

**Note** : 1. The presence of ferric salts can be tested by treating a few drops of solution with potassium thiocyanate. The formation of red coloration shows the presence of ferric salt. Addition of iron filings to the stage when no more of them dissolves will ensure the absence of ferric salts.

2. Crystals of ferrous sulphate can also be obtained from Kipp's waste, a solution of mainly ferrous sulphate containing unreacted sulphuric acid. Excess of sulphuric acid is consumed by adding iron filings. The other details are as given above. On concentrating the solution to the point of crystallization and cooling, pale green crystals of the hepta-hydrate are deposited.

**Result.** Colour of the crystals = ......

Shape = ......

Yield = ......

Percentage yield = ......

**Precautions.** Same as in Experments 2.1 and 2.3.

## ORAL QUESTIONS AND ANSWERS

**Q. 2.1.** What is the meaning of purity of a chemical substance ?

**Ans.** A pure substance is a single substance with definite melting point and other properties.

**Q. 2.2.** Explain the meaning of these words : solvent, solute, solution, soluble, saturated and crystals.

**Ans. Solvent.** It can keep the solute, *i.e.*, a soluble substance in solution. It is the major component of a solution.

**Solute.** A substance which disperses in the solvent. It is the minor component of a solution.

**Solution.** A homogeneous mixture of a solvent and solute.

**Soluble.** A substance is said to be soluble when it disperses into the solvent making a clear solution.

**Saturated.** A solution is said to be saturated which cannot dissolve the solute after a certain stage and at a given temperature. Here in the solution the dissolved solute is in equilibrium with the solid solute.

**Crystals.** Substances which have a regular arrangement of particles and thus a defiite geometric shape.

**Q. 2.3.** What is meant by crystallization ?

**Ans.** When a hot saturated solution of a salt is allowed to cool slowly, the salt starts separating out in the form of crystals. This process is known as crystallization.

**Q. 2.4.** Why do crystals form when hot solution is cooled ?

**Ans.** From hot solution, on cooling, initially some bits of salt come out. Around these bits, more of bits start depositing forming crystals.

**Q. 2.5.** Does hot water as compared to cold water dissolve more solute or less ?

**Ans.** Hot water dissolves more solute, because its tendency toward randomness increases because of the increased energy on heating.

**Q. 2.6.** Why is the solution not concentrated too much or evaporated to dryness in the preparation of crystals.

**Ans.** When the solution becomes very concentrated, it will spit out of the dish as steam is formed beneath semi-solid parts of the mixture. Also we get poor quality crystals.

**Q. 2.7.** What is seeding ?

**Ans.** Sometimes the process of crystallization becomes very slow. In such cases, a well shaped crystal of the salt is suspended in the concentrated solution. Around this crystal, more bits of salt deposit. This is known as seeding.

**Q. 2.8.** Which of the two techniques is more efficient : decantation or filtration.

**Ans.** Filtration is more efficient because it removes even the fine particles suspended in a liquid medium.

**Q. 2.9.** What is an unsaturated solution ?

**Ans.** An unsaturated solution is one which can take more of the solute at that temperature.

**Q. 2.10.** What is a crystal ?

**Ans.** The solid form of a particle having regular geometrical shape is named as crystal.

**Q. 2.11.** What is decantation ?

**Ans.** The process of separating insoluble substances from a liquid by simply allowing it to stand for some time and then pouring off the mother liquor.

**Q. 2.12.** What is distillation ?

**Ans.** The combined process of evaporation and condensation is termed as distillation.

**Q. 2.13.** What is evaporation ?

**Ans.** Evaporation is a process in which a liquid is converted into its vapour either by exposure to air at ordinary temperature or by the application of heat.

**Q. 2.14.** List the factors that influence solubility.

**Ans.** (*i*) Nature of the solute and solvent.

(*ii*) Temperature, and

(*iii*) Pressure.

**Q. 2.15.** What is mother liquor ?

**Ans.** The liquid which is left after crystals are separated from the saturated solution is called the mother liquor.

**Q. 2.16.** What is blue vitriol ?

**Ans.** Hydrated copper sulphate ($CuSO_4.5H_2O$) is known as blue vitriol.

**Q. 2.17.** Will the aqueous solution of copper sulphate be acidic, basic or neutral ?

**Ans.** It will be acidic.

**Q. 2.18.** What is green vitriol ?

**Ans.** Hydrated iron (II) sulphate, $FeSO_4.7H_2O$ is called green vitriol.

**Q. 2.19.** What is common ion effect ?

**Ans.** The common-ion-effect is the effect on a system at equilibrium caused by the addition of a substance with an ion common with one involved in the equilibrium.

**Q. 2.20.** How do you prepare HCl gas ?

**Ans.** Common salt on reacting with conc. $H_2SO_4$ gives HCl gas.

**Q. 2.21.** What is Kipp's waste ?

**Ans.** It is a solution of mainly ferrous sulphate with unreacted sulphuric acid in Kipp's apparatus in which $H_2S$ is produced by the reaction of iron (II) sulphide with dilute sulphuric acid.

**Q. 2.22.** Why do the green crystals of ferrous sulphate turn brown on exposure to air ?

**Ans.** Due to its oxidation to basic ferric sulphate.

$$\underset{\text{(Green)}}{4FeSO_4}+2H_2O+O_2 \longrightarrow \underset{\text{(Brown)}}{4Fe(OH)\,SO_4}$$

**Q. 2.23.** What is efflorescence ?

**Ans.** Certain substances on exposure to air lose their water of crystallization. This property of the substance is known efflorescence.

**Q. 2.24.** How will you calculate the % purity of substance (or percentage of each substance) in the mixture ?

**Ans.** By using the formula given below :

$$\% \text{ component}=\frac{\text{Grams of component}\times 100}{\text{Grams of sample}}$$

**Q. 2.25.** Calculate the theoretical weight of copper sulphate obtainable from a given amount of cupric oxide.

**Ans.** Theoretical weight of copper sulphate

$$=\text{Wt. of CuO}\times\frac{\text{Gram formula wt. of } CuSO_4.5H_2O}{\text{Gram formula wt. of CuO}}$$

$$\% \text{ yield}=\frac{\text{Wt. of } CuSO_4.5H_2O \text{ obtained}}{\text{Theoretical wt. of } CuSO_4.SH_2O \text{ from the given amount of CuO}}\times 100$$

**Q. 2.26.** What is potash alum ? Is it a double salt or complex compound ?

**Ans.** The chemical formula for potash alum is $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

Potash alum, add other alums, are double salts. Potash alum on dissolving into water furnishes $K^+$, $Al^{3+}$ and $SO_4^{2-}$ ions which can be tested by their usual tests.

**Q. 2.27.** What is the nature of aqueous solution of potash alum.

**Ans.** Acidic.

**Q. 2.28.** 'The crystals of alums grow easilry'. Comment on the statement.

**Ans.** Alums are sparingly soluble in cold water. Because of this property, their crystals grow easily.

**Q. 2.29.** How does potash alum help in the purification of water ?

**Ans.** Dust particles being negatively charged are coogulated by $Al^{3+}$ ions. As a result, the dust particles settle down making water clear.

**Q. 2.30.** How will you prepare a sample of potash alum in you laboratory ?

**Ans.** Dissolve the weighed $K_2SO_4$ ($\sim$2g) and $Al_2(SO_4)_3$ ($\sim$7g) in about 7 ml disstilled water contained in two separate beakers. Heat the solutions to boiling. Mix the two hot solutions. A double salt of potassium aluminium sulphate is thus produced. On cooling fine crystals of the alum separate. If necessary the solution can be concentrated.

□ □

# UNIT 3

# Study of Solubility of Solid Substances in Water

## 3.1. Introduction

A homogeneous mixture of two or more substances is called a **solution**. The substance which dissolves or disappears into the solution is called a **solute**. The other substance which dissolves the solute serves as the medium in which the solute is homogeneously dispersed, called the solvent. In a true solution, the dissolved solute particles will neither settle at the bottom of a container nor can they be filtered out by usual methods of filtration. The process of dissolving is commonly described as a physical change, because both the solute and solvent can be processed in their original forms by the evoporation of the solvent. For example, the crystals of copper sulphate give blue coloured solution when dissolved in liquid water. Simple evaporation of the water restores the original components of the solution.

$$CuSO_4(aq) \xrightarrow{\text{evaporation}} \underset{\text{Blue crystals}}{CuSO_4.5H_2O} + H_2O$$

From the knowledge of solution, we know that gases form homogeneous mixture in all proportions. Many liquids may also dissolve in other liquids in all proportions to give clear solutions, *e.g.* ethanol dissolves in water. On the other hand, there are many instances, when the solid substance dissolves into the solvent upto a certain limit. For example, at 18°C, no more than 35·9 g of sodium chloride will dissolve in 100 g of water. This means that 35·9 g of sodium chloride can be dissolved in 100 g of the solvent at 18°C to make a saturated solution. Such a limit is explained in terms of solubility.

**Solubility** may be defined as the amount of solute in grams that can be dissolved in 100 g of a solvent to obtain a saturated solution at a given temperature.

A solution that contains the maximum amount of a substance (solute) that can be dissolved in a given amount of the solvent at a specified temperature is called saturated solution. In such a solution the dissolved solute is in equilibrium with the solid solute. A solution, in which more of the solute can be dissolved at a specified temperature is known as unsaturated solution.

Usually, when the temperature is raised (*i e.* when the solution is heated) more solid can dissolve in water. If the temperature is then lowered, the extra solute will usually crystallize out of solution. Although the solubility of many substances in water increases with increasing temperature, as Fig. 3·2 illustrates, the solubility of some substances remains nearly constant or even decreases.

Heat is the one common factor that can affect the extent of the solubility of solid and liquid compounds. Grinding of large crystals into powder and violent stirring of the solvent during the dissolving process accelerate the solution process but do not increase the solubility of a substance.

## 3 2. Solubility Curve

For any specified temperature, the solubility of a solute in different solvents or of different solutes in a given solvent will have a characteristic set of values which change as temperature is changed. If a graph is plotted between the solubility of a solute in a given solvent and temperature data, the line thus obtained is known as **solubility curve**. A typical curve is shown in Fig. 3.1. The solubility curve can have various slopes and even shapes. The curve in Fig. 3.1 shows an increase in solubility with a rise in temperature. A set of solubility curves are shown in Fig. 3.2 for comparison.

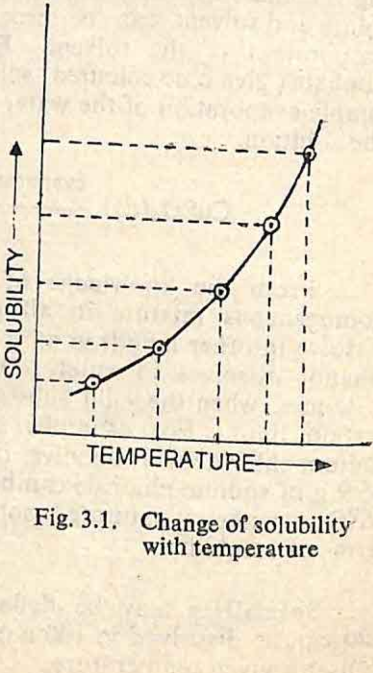


Fig. 3.1. Change of solubility with temperature

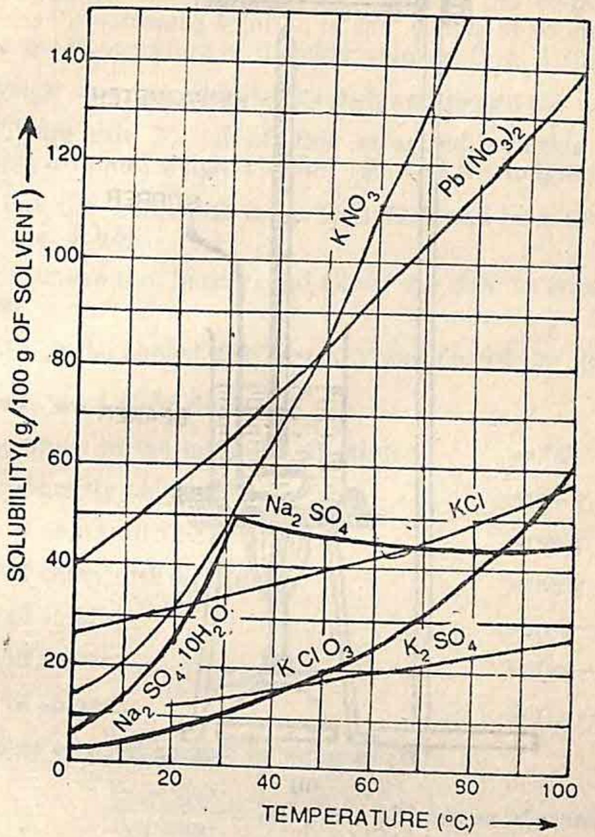


Fig. 3.2. Solubility curves of a few common substances

## 3.3 Experiments

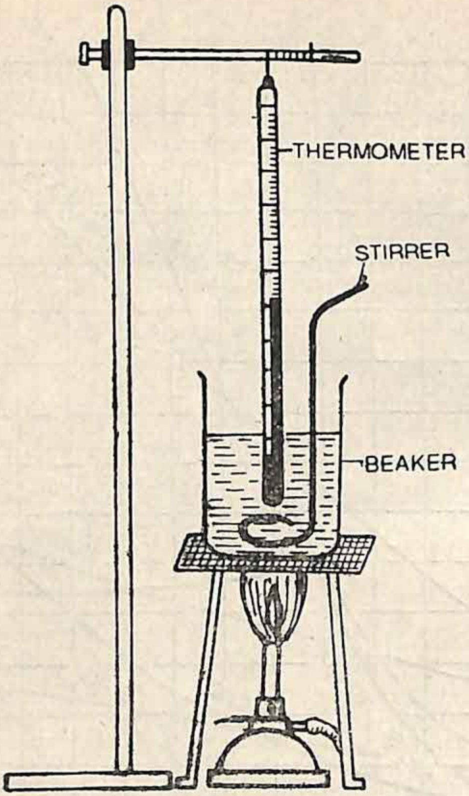
**Experiment 3.1.** To determine the solubility of a solid substance in water at room temperature.

**Apparatus.** China dish, funnel, glass rod, thermometer, beaker, pestle and mortar, pair of tongs, filter paper, funnel stand, water bath, balance, weight box, solid sample, 20 ml pipette, tripod stand, etc.

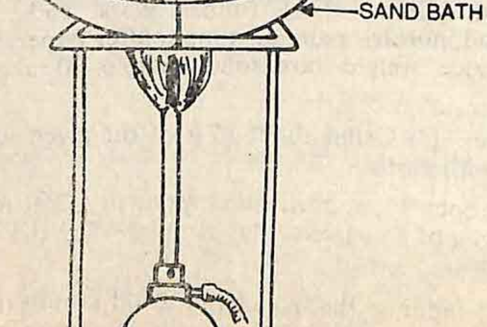
**Procedure.** (*i*) Grind about 25 g of the given solid sample in a clean mortar with pestle.

(*ii*) Take about 25 ml of distilled water in a 250 ml beaker and add to it about 5 g of powdered solid sample. Stir the contents with a glass rod.

(*iii*) Go on adding the powdered solid sample in instalments (about 2 g at a time) with stirring until no more of the solute dissolves in water and some of it remains undissolved.



(a)



(*iv*) Decant off the clear liquid or filter if the solution is not clear. This is the saturated solution of the sample at room temperature. Note the temperature of the clear solution [Fig. 3.3(*a*)].

(*v*) Weigh an empty clean china dish and record the weighing.

(*vi*) Pipette out 20 ml of this saturated solution into the weighed china dish and weigh it again. Record the weighing.

(*vii*) Put the china dish on a sand bath and heat the solution to dryness (Fig. 3.3(*b*)).

(*viii*) Remove the burner and allow the dish to cool at room temperature.

(*ix*) Weigh the cooled dish carefully and record the weighing.

**Observations and Calculations :**

Temperature of the saturated solution $= t°\text{C}$
Mass of empty china dish $= w_1\ g$
Mass of china dish+solution $= w_2\ g$
Mass of china dish+residue $= w_3\ g$
Mass of solution $= (w_2 - w_1)g$
Mass of solute $= (w_3 - w_1)g$
Mass of solvent $= (w_2 - w_3)g$

Solubility of solid sample in water at $t°$C

$$\frac{(w_3 - w_1)}{(w_2 - w_3)} \times 100 \text{ g per 100 grams of water}$$

**Result.** Solubility of the solid sample at $t°$C is

$$\frac{(w_3 - w_1)}{(w_2 - w_3)} \times 100 \text{ g per 100 g of water}$$

**Precautions.** (*i*) Weighing should be done carefully to obtain correct results.

(*ii*) While handling evaporating dish with a pair of tongs take care that the tip of the tongs does not touch the contents.

(*iii*) Keep the china dish with the residue in a desiccator for cooling.

*iv*) Ensure that the residue is completely dry before weighing.

(*v*) Residue in the dish should be heated, cooled and weighed again and again until a constant weight is obtained.

(*vi*) Always use water bath or sand bath for heating purposes to avoid spurting.

**Experiment 3.2.** To determine the solubility of potassium chloride at different temperatures and to plot the solubility curve.

**Apparatus and chemicals required.** Two beakers of 250 ml capacity, china dishes, funnel, funnel stand, filter paper, glass rod, water bath, pipette, pair of tongs, weight box, burner, match box, iron stand, wire gauze, pestle and mortar, a thermometer graduated to ½° centigrade, 100 ml measuring cylinder and potassium chloride.

**Procedure.** (*i*) Take about 100 g of potassium chloride and grind it with a pestle in a clean mortar.

(*ii*) Take a clean and dried 250 ml beaker. Pour about 50 ml of distilled water with the help of a measuring cylinder.

(*iii*) Place this beaker on a wire gauze resting on a tripod stand and suspend a thermometer in it graduated to ½°C, such that its bulb and a part of its stem is under water. [Fig. 3.3 (*a*)]

(*iv*) Heat the water in the beaker. Now pour about 25 g of the powdered potassium chloride in it by means of a paper spoon.

(*v*) Stir the solution well with a glass rod.

(*vi*) Go on adding about 5 g of powdered potassium chloride at a time until no more of it dissolves at 100°C. Put off the burner.

(*vii*) Now watch the fall in temperature.

(*viii*) When the temperature just reaches 90°C, take out 5 ml of the solution by means of a clean pipette and transfer it to a weighed china dish marked no. 1. Weigh it again and record the reading.

**Note.** The solution should be drawn off as quickly as possible lest there should be a further fall in temperature and deviation in the result.

(*ix*) Allow the main solution to cool to 80°C and immediately take out 5 ml of saturated solution and transfer it to another weighed china dish. Take out, the solution at different temperatures, say at an interval of 10°C in a number of preweighed china dishes, labelled 2, 3, 4, 5, 6. Weigh them separately and record the readings.

(*x*) Heat the solution contained in china dish 1 on a water bath to dry mass and cool the china dish to room temperature. Record the reading.

(*xi*) Similarly, heat the solutions contained in other china dishes numbered 2, 3, 4, 5 and 6 on a water bath to dry mass and cool them to room temperature. Determine the weight of each of the cooled dishes containing the dry substance and record the readings.

(*xii*) Heat, cool and weigh each dish until you get a constant weight.

(*xiii*) From the data thus obtained calculate the solubility of potassium chloride at different temperatures.

**Observations :**

Mass of empty china dish marked 1 $= w_1$ g
Mass of china dish + 5 ml solution $= w_2$ g
Mass of china dish + residue $= w_3$ g
Mass of residue $= (w_3 - w_1)$ g
Mass of solution $= (w_2 - w_1)$ g
Mass of solvent $= (w_2 - w_3)$ g
Temperature = 90°C

Repeat the mode of record of observations in the case of dishes at 80°C, 70°C, 60°C, 50°C etc.

**Calculations :**

$(w_2 - w_3)$ g of water dissolves $(w_3 - w_1)$ g solute

$\therefore$ 100 g of water will dissolve $= \dfrac{(w_3 - w_1)}{(w_2 - w_3)} \times 100$ g solute at 90°C.

Proceed in a similar way with dishes marked 2, 3, 4, 5, 6, etc..

**Record of the results :**

| *S. No.* | *Amount of KCl dissolved in 100 g of distilled water obtained by calculation* | *Temperature* |
|---|---|---|
| 1 | 54 g | 90°C |
| 2 | 50 g | 80°C |
| 3 | 46 g | 70°C |
| 4 | 42 g | 60°C |
| 5 | 40 g | 50°C |
| 6 | 38 g | 40°C |
| 7 | 34 g | 30°C |
| 8 | 21 g | 20°C |

Plot of a graph between temperature °C versus solubility (g/100 g of solvent) will give a curve as shown in Fig. 3.2 for potassium chloride.

**Experiment 3.3.** To study the variation of the solubility of potassium nitrate with temperature and to plot the solubility curve.

**Apparatus.** A boiling tube, beaker, thermometer, wire guaze, clamp stand, weight box, tripod stand, iron stand, glass rod, cork, etc.

**Chemical.** Potassium nitrate and distilled water.

**Procedure.** (*i*) Assemble the apparatus as shown in Fig. 3.4.

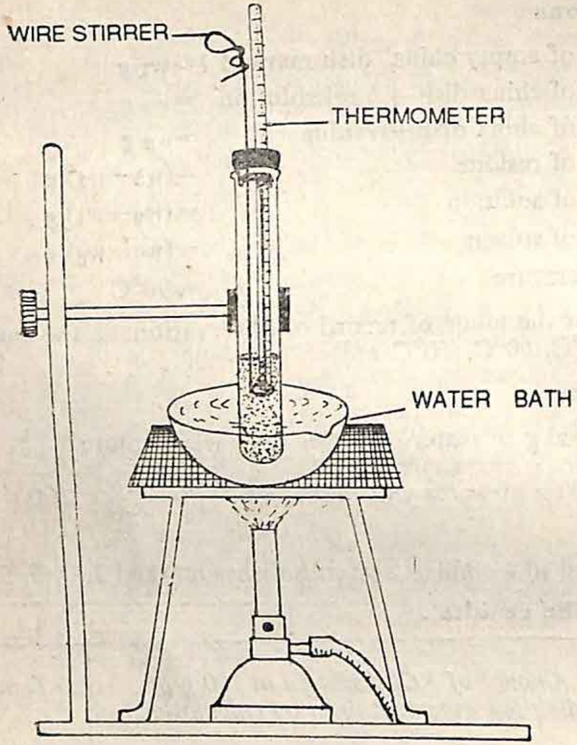


Fig. 3.4. Assembly for the determination of solubility of $KNO_3$ in water.

(*ii*) Take 25 ml of distilled water in the boiling tube, then add 15 *g* of powdered sample of potassium nitrate in it and cork it.

(*iii*) Heat the contents of boiling tube with stirring in a water bath to dissolve all the potassium nitrate. Record the temperature. Stop heating the water bath. Keep stirring the solution. Note down the temperature at which potassium nitrate starts separating. Take the mean of these two temperature readings.

(*iv*) Now add 5 *g* of correctly weighed potassium nitrate to the boiling tube, cork it and start heating with stirring until the whole of potassium nitrate dissolves. Note the temperature. Stop heating and keep stirring the solutions. Note down the temperature at which potassium nitrate reappears. Take the mean of two temperatures.

(*v*) Repeat the operation with three such additions of 5 *g* each. Record the temperature each time the salt dissolves completely, and also when the crystals of potassium nitrate reappear. Take the mean of the two temperatures in each case.

(*vi*) From the data of the expetiment, calculate the amount of potassium nitrate dissolved in 100 g solvent at various temperatures.

(*vii*) Now draw the graph between the solubility data of potassium nitrate and temperature. A graph similar to that shown in Fig. 3.5 will be obtained.

**Observations :**

Amount of water taken in a boiling tube=25 ml
(∵ 1 ml of water weighs 1 *g*) =25 *g*

| *S.No.* | *Amount of $KNO_3$ dissolved* | *Amount of $KNO_3$ dissolved in 100 g distilled water* | *Temperature at which $KNO_3$ dissolves completely $t_1$°C* | *Temperature at which $KNO_3$ separates on cooling t°C* | *Mean temperature* |
|---|---|---|---|---|---|
| 1 | 15 *g* | 60 *g* | | | |
| 2 | 20 *g* | 80 *g* | | | |
| 3 | 25 *g* | 100 *g* | | | |
| 4 | 30 *g* | 120 *g* | | | |
| 5 | 35 *g* | 140 *g* | | | |

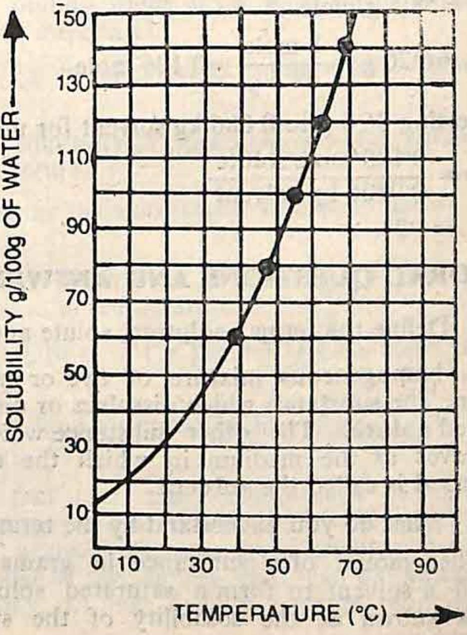


**Fig. 3.5. Solubility curve of potassium nitrate.**

**Experiment 3.4.** From the determination of the solubility of common salt in water, find out the molality of its saturated solution at room temperature.

**Hint.** A molal solution, represented by *m*, is one in which there is a concentration of one mole of solute per kilorgram of solvent.

$$\text{Molality}=\frac{\text{moles solute}}{\text{kg solvent}}$$

Find out the solubility of common salt at room temperature as suggested in experiment 3.1. Suppose this solubility is *S* which will correspond to the maximum weight of the solute in grams that will dissolve in 100 g of water at room temperature. Therefore, the molality of the saturated solution will be

$$=\frac{\text{moles of NaCl}}{\text{kg solvent}}$$

$$=\frac{S/58{\cdot}5}{100/1000}=\frac{S}{58{\cdot}5}\times\frac{1000}{100}$$

(Molculer weight of sodium chloride=58·5)

**Exercise 3.1.** What is the molality of a solution in which 6·20 g of NaCl(s) is dissolved in 86·0 g of water ?

**Solution.** It is necessary to calculate the moles of NaCl

$$\text{NaCl}=58{\cdot}5\ \text{g/mole}$$

$$n=6{\cdot}20\ \text{g}\times\frac{1\ \text{mole}}{58{\cdot}5\ \text{g}}=0{\cdot}106\ \text{mole}$$

By converting 86·0 g to 0·086 kg solvent for molality

$$m=\frac{0{\cdot}106\ \text{mole solute}}{0{\cdot}0806\ \text{kg solvent}}$$

$$=1{\cdot}23.$$

## ORAL QUESTIONS AND ANSWERS

**Q. 3.1.** Define the terms : solution, solute and solvent.

**Ans.** A homogeneous mixture of two or more substances is called **solution**. The substance which dissolves or disappears into the solution is called **solute**. The other substance which dissolves the solute and serves as the medium in which the solute is homogeneously dipersed is called the **solvent**.

**Q. 3.2.** What do you understand by the term solubility ?

**Ans.** Thea mount of a substance in grams which dissolves in 100 grams of a solvent to form a saturated solution at a known temperature is known as the solubility of the substance in that solvent.

**Q. 3.3.** Define a saturated solution.

**Ans.** A solution which remains in equilibrium with undissolved solute for any length of time at a temperature without experiencing any change (decrease or increase) in concentration.

**Q. 3.4.** How will you express the solubility of a substance ?

$$\text{Solubility} = \frac{\text{Weight of solute in a certain quantity of saturated solution}}{\text{Weight of solvent in the same quantity of saturated solution}} \times 100$$

**Q. 3.5.** What is a solubility curve ?

**Ans.** A graph plotted between the solubility of a solute in a given solvent and the temperature data is called a solubility curve.

**Q. 3.6.** What is the effect of temperature on the solubility of solid substances ?

**Ans.** The solubility of solid substances, in general, increases with the increase of temperature. However, in some cases, the solubility decreases with increase of temperature (*e.g.* the solubility of $Na_2SO_4$ decreases with rise of temperature, Fig. 3.2).

**Q. 3.7.** What happens to the boiling point of a solvent containing some dissolved impurity ?

**Ans.** The boiling point of a solvent increases in the presence of the soluble impurities.

**Q. 3.8.** What is the effect of temperature on the solubility of gases ?

**Ans.** The solubility of gases, in general, decreases with the increase of temperature.

**Q. 3.9.** Name the substances whose solubility is affected by the temperature.

**Ans.** (*i*) The solubilities of $AgNO_3$, $KNO_3$ & KCl increase rapidly with increase in temperature.

(*ii*) The solubilities of CaO and KOH decrease with increase in temperature.

**Q. 3.10.** Why does the solubility of most solids increase with a rise in temperature ?

**Ans.** The fact that many compounds increase in solubility when heated relates to the tendency toward randomness. Most solutions, when heated, increase their tendency toward increased randomness because of the energy that can be absorbed. For this reason, the supply of heat usually permits more of the solid to dissolve.

If the dissolution of a substance is accompanied with the evolution of heat, the solubility decreases because of the decrease in randomness.

**Q. 3.11.** Two flasks contain a saturated and an unsaturated solution of the same substance respectively. How will you determine which flask contains which solution ?

**Ans.** A flask in which there is no undissolved salt contains unsaturated solution. Also it can be ascertained by adding more of the substance to both the flasks. If the added sample in the flask *A* disappears, the solution in flask A is unsaturated. However, if the sample does not disappear, the solution is saturated.

**Q. 3.12.** From the determination of the solubility of common salt in water. Find out the molality of its saturated solution at room temperature.

**Ans.** Suppose the solubility of the common salt at room temperature is S *g*/100 g of water.

∴ Molality of the saturated solution will be

$$\frac{S}{58{\cdot}5} \times \frac{1000}{100}$$

(Molecular wt. of NaCl is 58·5).

**Q. 3.13.** How will the solubility of $Na_2SO_4.10\,H_2O$ be affected by a change of temperature ? Why does the solubility curve of this compound has a point of inflection and what does it designate ?

**Ans.** At lower temperature say upto 32·5°C the solubility of $Na_2SO_4.10H_2O$ increases with increase in temperature and above 32·5°C the solubility decreases with increase in temperature. The inflection (discontinuity) is due to the change in the composition of the salt. If a solution of sodium sulphate is cooled, the solid separating at lower temperatue is the decahydrate and the solid separating at the higher temperature is the anhydrous salt (Fig. 3.2). There are, therefore, two solubility curves of two solutes. The breaking point is called the transition point.

**Q. 3.14.** State what is likely to happen when the followings are boiled ?

(*a*) water containing dissolved air

(*b*) dil. KCl solution

(*c*) dil. HCl solution.

**Ans.** (*a*) Air will evolve—it indicates air is more soluble in cold water than in hot water.

(*b*) Solubility will increase.

(*c*) HCl gas will be evolved—gases are less soluble in hot solution than in cold solution.

**Q. 3.15.** What factors influence the solubility of

(*a*) A solid, and

(*b*) A gas in water ?

**Ans.** (*a*) Depends upon temperature, nature of the solid and pressure.

(*b*) Depends upon temperature, pressure and nature of the gas.

**Q. 3.16.** Is there any effect of impurity on the solubility of a substance ?

**Ans.** Solubility is affected by the presence of impurity. For example, the presence of hydrochloric acid reduces the solubility of sodium chloride, magnesium chloride, etc.

**Q. 3.17.** Does pressure affect the solubilitly of a solid ?

**Ans.** Not affected appreciably by pressure.

**Q. 3.18.** Explain why does pulverizing of a solid solute increase the rate of dissolution ?

**Ans.** Pulverizing of a solid into powder and vigorous stirring of the solvent during the dissolving process increase the rate of solution process, but do not increase the solubility of the solute. These operations allow more surface of the solute to come in contact with the water dipoles within a given time.

**Q. 3.19.** Why does stirring increase the rate at which most solids dissolve ?

**Ans.** See the answer of Q. 3.18.

**Q. 3.20.** What is the nature of the process of dissolving a solid in solvent.

**Ans.** It is a physical change. Both the solute and solvent can be processed in their original forms.

□ □

# UNIT 4

# Separation and Purification of Solid Components

## 4.1. Introduction

The meaning of purity in the context of chemistry has already been discussed in Unit 2. In that unit, the technique of crystals formation has also been explained. There are different methods which can be employed for the separation of constituents of a mixture. Mixture of solid components could be of two types—homogeneous and heterogeneous. The melting point and solubility are the two major properties of the components of the mixtures which are being made the basis of their separation. Fractional crystallization is one of the purification techniques which depends upon the different solubilities of the substances in a mixture in a solvent.

To get substances pure further recrystallization is often necessary. Sublimation is another technique of purifying a mixture of compounds, in which one sublimes, but the other does not. These two processes for the separation and purification of substances are described below.

## 4.2. Fractional Crystallization

Solubility curves (Unit 3) tell us about the relative solubility of various substances at a given temperature say at room temperature or other temperatures. In separating the two components of a mixture, the relative difference in their solubility is exploited. Usually the solubilities of the substances in a mixture are such that a mixture of the substances is deposited on cooling, but the composition of the mixture will be different from that of the solution. This is the basis of a method of separation of a mixture of solids known as fractional crystallization. In a particular difficult case, where a mixture of two components has been separated by this means into, say, ten fractions, perhaps the first two fractions contain exclusively one component and the last two exclusively the other, with the interevning six mixtures of varying composition. Those which are rich in one component may be purified by simple recrystallization and those which are not may be combined and refractionated. To get substances pure, further recrystallization of various crops of crystals including the purer crops are often necessary. This makes fractional crystallization a very tedious process, but it is a valuable method used for obtaining pure substances from mixtures.

Factors like concentration, temperature and solvent composition help in controlling the fractionation.

*Concentration.* One can make up the initial solution in a good deal more than the minimum amount of boiling solvent in order to ensure that only a small quantity of solid separates on cooling. After collecting the first crop, the mother liquor can be concentrated a little, by evaporating off some solvent and allowed to cool and produce a second crop of crystals. Further crops can be obtained in the same way.

*Temperature.* It can be made use of by collecting the crystals which separate from a solution at successively lower temperatures.

*Solvent composition.* First one can start with a pure solvent and collect the first crop of crystals. After this, add to the mother liquor small quantities of a second solvent, thus altering the solvent composition, and collecting the crystals which separate after each successive addition.

In this technique the mixture (or impure product) is first dissolved in a small amount of hot solvent (generally one in which the desired product (A) is less soluble than the other (B). As the hot solution is allowed to cool, the product A separates form the mixture, leaving the substance 'B' behind. The quantity of product 'A' that can be recovered in this fashion depends on the concentration of 'B' and its solubility relative to that of A.

The purification of substances by fractional crystallization is something of an art, which can be learned only through repeated practice.

### 4.3. Sublimation

There are some solids whose boiling points fall below their melting points, and as they are heated, when the appropriate temperature is reached they change straight from the solid state into the vapour state. On cooling, the vapour transforms back to the solid state, without becoming a liquid, usually as well-formed crystals. This forms the basis of an excellent mean of purifying some solids, and is known as sublimation. This process can be used to purify a mixture of compounds in which one sublimes, but the other does not. Relatively few solids have this property of subliming. However, because so few solids can sublime, the probability of impurities subliming with the compound being purified is reduced and thus the method more likely to succeed.

In a mixture of *ammonium chloride* and *sodium chloride*, ammonium chloride is a volatile component. This mixture is taken in a china dish and is covered with an inverted funnel as shown in Fig. 4.1. The stem of the funnel is plugged with cotton wool. The solid deposited on the inner side of the funnel is collected. The non-volatile sodium choride is left in the dish.

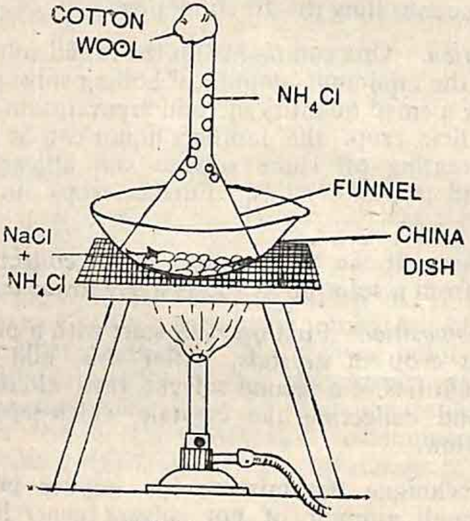


Fig. 4.1. Sublimation

## 4.4. Experiments

**Experiment 4.1**. To separate a mixture of ammonium chloride and sodium bicarbonate by fractional crytallization.

**Apparatus**. Beakers, funnels, glass rods, filter papers, evaporating dish, funnel stand, tripod stand, wire guaze, burner, pestle and mortar.

**Chemicals**. Mixture of ammonium chloride and sodium bicarbonate.

**Solubility Information**. The separation is accomplished by knowing the solubility of both $NH_4Cl$ and $NaHCO_3$ in water. The literature values are as follows :

| Substance | 0°C | 20°C | 60°C | 100°C |
|---|---|---|---|---|
| $NH_4Cl$ | 29.3 | 37.2 | 55.2 | 77.3 |
| $NaHCO_3$ | 6.9 | 9.0 | 16.4 | |

In case the solubility data is not available, the solubility of the components of the mixture is determined (Unit 3) in water at different temperatures. From the solubility curve one can find the solubility at different temperatures.

**Procedure.** (*i*) Put 15 *g* of the mixture of ammonium chloride and sodium bicarbonate in a small amount of water, say 25 ml, contained in a beaker.

(*ii*) Now heat the contents with stirring say upto 60°C.

(*ii*) When the solution is clear, add more of the mixture, while the contents are still being heated. Continue to add more of the mixture until no more mixture dissolves say at 60°C. Now heat the contents until the solution becomes clear. Filter hot.

(*iv*) As the hot solution is allowed to cool, the pure product, sodium bicarbonate starts separating from the mixture, leaving ammonium chloride behind. Keep collecting the samples at different temperatures say at 50°, 40°, 35°, 30°, 25°, 20°C. The first two samples are likely to be rich in $NaHCO_3$; the last two samples are likely to be rich in $NH_4Cl$; and the samples collected at 30°C and 35°C are expected to contain mixture of varying composition.

(*v*) Now purify the first two and the last two samples by recrystallization. Mix up the remaining two samples and repeat the process of fractional crystallization.

(*vi*) Finally collect the crystals of sodium bicarbonate and ammonium chloride and dry them.

**Results.** Yield of each component=......

Percentage yield of each component=......

**Precautions.** Same as in Experiment 2.1 (Unit 2).

**Note.** It is desired to have the necessary solubility data of the components of the mixture.

**Experiment 4.2.** To separate the mixture of alum say potash alum and copper sulphate by fractional crystallization.

**Apparatus.** Same as in Experiment 4.1.

**Chemicals.** A mixture of potash alum and copper sulphate.

**Solubility Information.** Alums are double salts and in solution potash alum is indistinguishable from a mixture of potassium and aluminium sulphates, *i.e.*, it contains potassium ions, aluminium ions, and sulphate ions, just as a mixture of the individual salts would do.

Solubility taken from the literature is as follows :

| Compound | 0°C | 20°C | 60°C | 100°C |
|---|---|---|---|---|
| Copper sulphate | 14·3 | 20·7 | 40·0 | 75·4 |
| Potash Alum | 5·7 | 10·0 | 20·0 | |

**Procedure.** The procedure followed is the same as in Experiment 4.1.

As the hot solution is allowed to cool, the pure product, potash alum starts separating from the mixture, leaving copper sulphate still in the solution. Collect the samples at different temperatures say at 50°, 40°, 35°, 30°, 25°, 20°C and purify them by simple crystallization as suggested in Unit 2.

**Result**. Yield of each component=......

Percentage yield of each component=......

**Precautions**. Same as in Experiment 2.1 (Unit 2).

**Experiment 4 3**. To separate a mixture of naphthalene and common salt.

**Apparatus**. Funnel, sand bath, water bath, china dish, tripod stand, burner.

**Chemical**. Mixture of naphthalene and common salt.

**Procedure**. (*i*) Take $\sim 10\ g$ mixture of naphthalene and common salt in a china dish.

(*ii*) Put the china dish on a sand bath and cover it with an inverted funnel as shown in Fig. 4.1. Plug it with cotton wool.

(*iii*) Now start heating the contents in the china dish. After a while, dense white fumes will start forming in the china dish, which will cool down and deposit on the inner walls of the funnel in due course. Collect the deposited sample of naphthalene.

(*iv*) The non-volatile common salt will be left in the dish.

**Result**. Yield of each component=......

Percentage yield of each component=......

## ORAL QUESTIONS AND ANSWERS

**Q. 4.1.** What is fractional crystallization ?

**Ans.** See Section 4.2 of this unit.

**Q. 4.2.** What is sublimation ?

**Ans.** See Section 4.3 of this unit.

**Q. 4.3.** State the principle involved in the fractional crystallization.

**Ans.** See Section 4.2 of this unit.

**Q. 4.4.** How is vapour pressure of solids related with the phenomenon of sublimation ?

**Ans.** A solid exerts a vapour pressure, although this vapour pressure is often very small because very few molecules in a solid normally have enough energy to break loose from the solid to form vapours. If a solid has a high vapour pressure, sublimation is adopted for the purification of substances.

**Q. 4.5.** Describe how you would obtain

(*i*) ammonium chloride from a mixture of ammonium chloride and common salt, and

(*ii*) Iodine from a mixture of iodine and sulphur ?

**Ans.** (*i*) By sublimation

(*ii*) By sublimation.

□ □

# UNIT 5

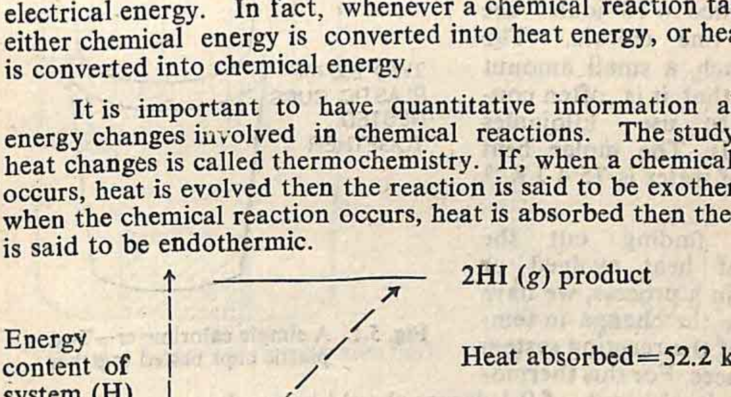
# Thermochemistry

## 5.1. Introduction

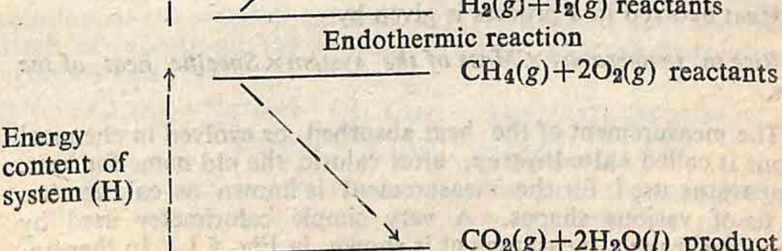
Almost all chemical reactions occur with either an absorption or a release of energy, depending on whether the energy stored in the products is greater or less than the energy stored in the reactants. The energy stored in chemical substances is called chemical energy. In turn, chemical energy is the energy associated with the breaking and formation of chemical bonds in a chemical reaction.

The energy released or absorbed in chemical reactions is usually observed in the form of heat but very occasionally as light and electrical energy. In fact, whenever a chemical reaction takes place either chemical energy is converted into heat energy, or heat energy is converted into chemical energy.

It is important to have quantitative information about the energy changes involved in chemical reactions. The study of these heat changes is called thermochemistry. If, when a chemical reaction occurs, heat is evolved then the reaction is said to be exothermic. If, when the chemical reaction occurs, heat is absorbed then the reaction is said to be endothermic.



Endothermic reaction


Energy content of system (H)
$CH_4(g)+2O_2(g)$ reactants
$CO_2(g)+2H_2O(l)$ product

Exothermic reaction

## 5.2. Heat Changes in Chemical Reactions and their Measurement

Heat is energy that is transferred as the result of a temperature difference. Heat is always given by a warmer object to a colder object. At the molecular level, molecules of the warmer object collide with those of colder object. During the course of collision, the molecules of the warmer object, which have a higher kinetic energy, lose kinetic energy to those of colder object. Heat flows between the two objects until they reach the equilibrium temperature.

The heat required to raise the temperature of an object or of a given amount of a substance by 1 kelvin is called the heat capacity of the object or of the particular amount of substance. The heat required to raise the temperature of 1 mole of a substance by 1 kelvin is the molar heat capacity of the substance. 4·18 joules are needed to raise the temperature of 1 g of water by 1 kelvin, hence 4·18 joules are equal to one calorie. The joule is such a small amount of energy that it is often convenient to use kilojoules (symbol kJ). The molar heat capacity of water is 75·4 J $K^{-1}$ $mol^{-1}$.

For finding out the amount of heat evolved or absorbed in a process, we have to measure the change in temperature of the reacting system or substances. For this thermometer with least count of 0.1 degree should be used.

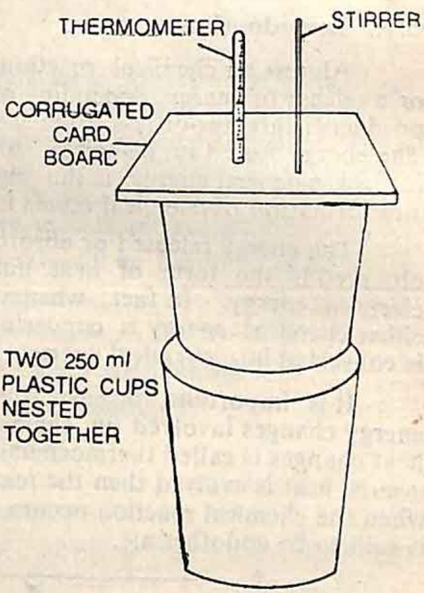


**Fig. 5.1. A simple calorimeter—Two plastic cups nested together**

Heat evolved in a process is given by—

*Rise in temperature × Mass of the system × Specific heat of the system.*

The measurement of the heat absorbed or evolved in chemical reactions is called **calorimetry**, after caloric, the old name for heat. The apparatus used for the measurement is known as calorimeter. It can be of various shapes. A very simple calorimeter used by students for rough measurement is shown in Fig 5.1. In thermochemistry Dewar flasks and thermos flasks (Fig. 5.2) are used. This type of calorimeter is suitable for making accurate measurements on reactions occurring in solution. Sometimes a reaction is carried out in a beaker placed in a thermally insulated box (Fig. 5.3).

## 5.3. Heat of Neutralization

The heat of neutralization of an acid with an alkali is the heat change which takes place when an acid is neutralized by an alkali. The reaction is carried out in dilute aqueous solution. It is the quantity of heat evolved when 1 mole of $H^+$ ions (*i e.* 1 g) reacts with 1 mole of $OH^-$ ions (*i.e.*, 17 g), to form 1 mole of water (*i.e.* 18 g).

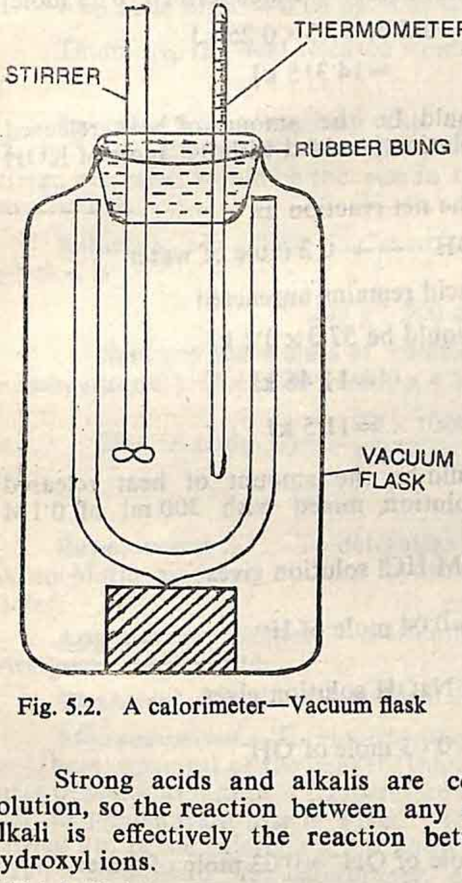


Fig. 5.2. A calorimeter—Vacuum flask

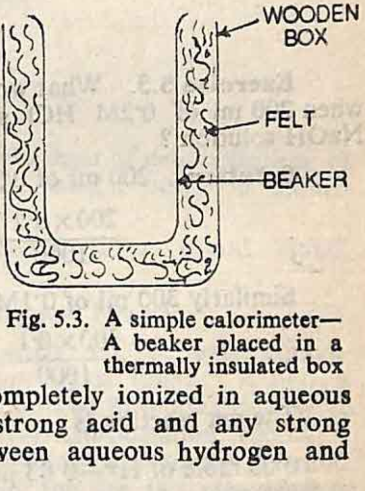


Fig. 5.3. A simple calorimeter—A beaker placed in a thermally insulated box

Strong acids and alkalis are completely ionized in aqueous solution, so the reaction between any strong acid and any strong alkali is effectively the reaction between aqueous hydrogen and hydroxyl ions.

$$H^+(s)+Cl^-(aq)+Na^+(aq)+OH^-(aq) \longrightarrow NaCl(aq)+H_2O(l)+57.3 \text{ kJ}$$

or $$H^+(aq)+OH^-(aq) \longrightarrow H_2O(l)+57.3 \text{ kJ}$$

This is established by the fact that the heat of neutralization of any strong acid by any strong alkali is approximately constant at 298 K, *i.e.* $\Delta H\ (298\ K) = -57.3\ kJ\ mol^{-1}$. If a weak acid or alkali is used or if both are weak, then the heat of neutralization differs significantly from the value given above. This is because weak acids and alkalis ionize only slightly in aqueous solution.

The following exercises will make the definition more clear.

**Exercise 5.1.** What would be the amount of heat released when 0·25 mole of HCl in solution is neutralized by 0·25 mole of NaOH solution ?

**Solution.** 0·25 mole HCl (*aq*)+0·25 mole NaOH (*aq*)

The net reaction is

$H^+$ (0·25 mole)+$OH^-$ (0·25 mole)⟶water formed (0·25 mole)

Therefore, heat released would be $57 \cdot 3 \times 0 \cdot 25$ kJ

$=14 \cdot 315$ kJ

**Exercise 5.2.** What would be the amount of heat released when 0·5 mole of nitric acid solution is mixed with 0·2 mole of KOH solution ?

**Solution.** In this case the net reaction is,

0·2 mole $H^+$+0·2 mole $OH^-$ ⟶ 0·2 mole of water

0·3 mole of $H^+$ of nitric acid remains unreacted

Therefore, heat evolved would be $57 \cdot 3 \times 0 \cdot 2$ kJ

$=11 \cdot 46$ kJ

$=11 \cdot 5$ kJ

**Exercise 5.3.** What would be the amount of heat released when 200 ml of 0·2M HCl solution mixed with 300 ml of 0·1M NaOH solution ?

**Solution.** 200 ml of 0·2M HCl solution gives

$$\frac{200 \times 0 \cdot 2}{1000} = 0 \cdot 04 \text{ mole of } H^+$$

Similarly 300 ml of 0·1M NaOH solution gives

$$\frac{300 \times 0 \cdot 1}{1000} = 0 \cdot 03 \text{ mole of } OH^-$$

The net reaction is :

0·03 mole of $H^+$+0·03 mole of $OH^-$=0·03 mole of water

Therefore heat released would be $0 \cdot 03 \times 57 \cdot 3$ kJ

$=1 \cdot 719$ kJ

$=1 \cdot 72$ kJ

**Exercise 5.4.** What would be the amount of heat released when 400 ml of 0·2M $H_2SO_4$ is mixed with 600 ml of 0·1M NaOH solution ?

**Solution.** 400 ml of 0·2M $H_2SO_4$ gives

$$=\frac{2\times0{\cdot}2\times400}{1000}\text{ mole of }H^+$$

$$=0{\cdot}16\text{ mole of }H^+$$

600 ml of 0·1M NaOH gives $\frac{600\times0{\cdot}1}{1000}=0{\cdot}06$ mole of $OH^-$

The net reaction is :

0·06 mole of $H^+$ + 0·06 mole of $OH^-$ = 0·06 mole of water

Therefore, the heat released would be 0·06 × 57·3

$$=3{\cdot}438\text{ kJ}$$

**Exercise 5.5.** Assuming the specific heat of water as 4·2 $JK^{-1}g^{-1}$ and ignoring the heat absorbed by container, thermometer, stirrer, etc. what would be the rise in temperature of the solution in exercise 5.3.

**Solution.** As given in exercise 5.3, approximate mass of solution is

$$200\text{ g}+300\text{ g}=500\text{ g}$$

∴ Heat evolved = mass of solution × sp. heat of solution × rise in temperature $1{\cdot}72\times1000\text{ J}=500\times4{\cdot}2\times t^\circ$

or Rise in temp. $(t)=\frac{1{\cdot}72\times1000}{500\times4{\cdot}2}$

$$=0{\cdot}82\text{ K}$$

**Experiment 5.1.** To determine the heat of neutralization of hydrochloric acid and sodium hydroxide using a beaker as calorimeter.

**Apparatus.** Beakers, thermometers, stirrer, tripod stand, wire guaze, burner, etc.

**Chemical.** Molar solutions of HCl and NaOH.

**Measurement.** It involves two steps : (I) The water equivalent (heat capacity) of the beaker (calorimeter) is found. A known mass of water at a known temperature is poured into the calorimeter and the temperature rise is noted. (II) A neutralization reaction is carried out in the calorimeter. Known volumes of standard acid and alkali are added to the calorimeter, and the rise in temperature is noted.

Water equivalent of a calorimeter is the amount of heat required to raise the temperature of the calorimeter by 1°C. (1 kelvin). In case of a glass vessel, the water equivalent value is found for such part of the vessel as is actually in contact with the reacting system. In this case, the usual method of obtaining the water equivalent by multiplying together the mass and specific heat of the material of the vessel is not practicable. The water equivalent of a glass vessel is found by carrying out an experiment similar to the experiment to be performed later in the vessels. As far as possible equal volumes are used so that surface area of calorimeter in contact with the system do not change.

**Step I. Determination of water equivalent of a calorimeter (beaker).**

**Procedure.** (*i*) Set up the apparatus shown in Fig. 5.3. Put 250 ml beaker in the thermally insulated box so that the beaker neither loses nor gains heat from the atmosphere.

Wait until the beaker attains the room temperature. Record this temperature.

Take 100 ml of distilled water in it.

(*ii*) Measure another 100 ml of distilled water in another 250 ml beaker. Cover it with a watch glass and heat.

When the temperature of water is raised by 15°C above the room temperature, stop heating and note the temperature of the hot water and pour this hot water quickly in the beaker kept into the thermally insulated box.

(*iii*) Stir the mixture gently and note the final temperature of the mixture.

**Step II. Determination of heat of neutralization.** Take 100 ml of 1 M hydrochloric acid in a calorimeter (for which water equivalent has been determined). Note the temperature of the acid when it becomes steady. Add 100 ml of 1M sodium hydroxide (at the same temperature) to it. Stir the mixture well and note the final temperature.

**Precautions :**

(*i*) Temperature should be noted correctly.

(*ii*) While stirring liquid should not spurt.

(*iii*) The calorimeter should be insulated as perfectly as possible (Fig. 5.3).

(*iv*) The two thermometers used for two solutions should be compared before use.

**Observations :**

Mass of cold water taken $= 100$ g
Temperature of cold water $= t_c$ °C
Mass of hot water $= 100$ g
Temperature of hot water $= t_h$ °C
Temperature of the mixture $= t_m$°C
Temperature of acid or alkali solution $= t_1$° C

Temperature after mixing acid and alkali solutions $= t_2$° C

Mass of acid or alkali solution $= 100$ g

Heat capacity of water $= 4{\cdot}18$ J

**Calculations :**

**(1) Calculation of water equivalent of calorimeter**

Let the water equivalent of calorimeter (beaker) be W g.

Heat lost by hot water $= m \times s \times \theta$

$$m = 100 \text{ g}$$

$$s = 4{\cdot}18 \text{ J for water}$$

$$\theta = (t_h - t_m)$$

∴ Heat lost by hot water $= 100(t_h - t_m) \times 4{\cdot}18$ J/deg

Heat gained by calorimeter (beaker)+cold water

$$= [W(t_m - t_c) + 100\,(t_m - t_c)\,4{\cdot}18] \text{ J/deg}$$

Heat gained = Heat lost

$$W(t_m - t_c) + 100(t_m - t_c)4{\cdot}18 = 100(t_h - t_m) \times 4{\cdot}18$$

$$(W + 100 \times 4{\cdot}18)(t_m - t_c) = 100(t_h - t_m) \times 4{\cdot}18$$

$$(W + 100 \times 4{\cdot}18) = \frac{100(t_h - t_m) \times 4{\cdot}18}{(t_m - t_c)}$$

$$W = \left(100 \times 4{\cdot}18 \;\; \frac{(t_h - t_m)}{t_m - t_c} - 100 \times 4.18\right) \text{J/deg}$$

**(2) Calculation of heat of neutralization**

Rise in temperature of alkali or acid solution after mixing the two

$$= (t_2 - t_1)^\circ\text{C}$$

Heat evolved when the two solutions are mixed

= Heat gained by calorimeter + Heat gained by solution

$$Q = [W(t_2 - t_1) + 200(t_2 - t_1) \times 4{\cdot}18] \text{ J}$$

$$= [(W + 200 \times 4{\cdot}18)(t_2 - t_1) \text{ J}$$

Here the specific heats of acid and alkali solutions are taken as that of water. Influences of increased density and decreased specific heat almost cancel each other.

Further by calculating the amount of water formed, the standard heat of neutralization can be expressed in terms of kJ $\text{mol}^{-1}$.

Now in 100 ml 1M HCl there is $\frac{100 \times 1}{1000}$ mole HCl

$= 0{\cdot}1$ mole HCl

(in a similar way, there is 0·1 mole NaOH)

The equation for the neutralization is,

$$HCl(aq)+NaOH(aq) \longrightarrow NaCl(aq)+H_2O(l)$$

Accordingly, one mole of HCl produces one mole of water,

Thus 0·1 mole HCl will produce 0·1 mole of water.

The amount of heat evolved in producing 0·1 mole of water is $x$J.

∴ 1 mole of water will be produced with the evolution of

$$\frac{x}{0{\cdot}1} \text{ J heat energy}$$

$$= \frac{x}{0{\cdot}1 \times 1000} \text{ kJ} = \frac{x}{100} \text{ kJ}$$

**For approximate calculations, water equivalent of the calorimeter may be neglected.*

**Result.** The value of heat of neutralization is $\frac{x}{100}$ kJ $mol^{-1}$.

## 5.4. Heat of Solution

Energy is usually evolved or absorbed when a substance dissolves in water (or solvent). This heat change is called the heat of solution and it is the quantity of heat evolved or absorbed when 1 mole of a substance is dissolved in sufficient water (or an infinite amount of solvent) so that no further heat change occurs on dilution.

There are several reasons why heat changes occur when a substance dissolves. When an ionic solid dissolves in a solvent, two enthalpy terms are involved.

1. The ions must be separated from the ionic lattice. To do this, the energy required is the lattice dissociation energy. This is an endothermic process.

2. The separate ions interact with the molecules of the solvent. If the solvent is polar, a charged ion can be attracted to one end of a polar solvent molecule *i.e.* when it dissolves in solvent become solvated. Solvation (or hydration) liberates energy. The energy released compensates for the energy required to dissociate the lattice.

$$\underset{\text{(or Dissolution)}}{\Delta H_{solution}} = \underset{\text{(a positive quantity)}}{\Delta H_{lattice\ dissociation}} + \underset{\text{(a negative quantity)}}{\Delta H_{solvation}}$$

If $\Delta H_{dissolution}$ is negative, dissolution is favoured by enthalpy considerations. If $\Delta H_{dissolution}$ is positive, dissolution may still occur endothermically if it is favoured by entropy considerations.

Consider the dissolution of sodium hydroxide, ammonium nitrate and sodium chloride in water.

The dissolution of NaOH in water is exothermic because the hydration energy exceeds the energy of lattice dissociation.

$$NaOH(s)+H_2O(l) \longrightarrow Na^+(aq)+OH^-(aq)$$

The dissolution of $NH_4NO_3$ in water is endothermic because the energy required to separate the ammonium ions and nitrate ions in solid is far greater than the hydration energy.

$$NH_4NO_3(s)+H_2O(l) \longrightarrow NH_4^+(aq)+NO_3^-(aq)$$

The dissolution of sodium chloride is said to be thermoneutral. This is because the energy required to break up the solid NaCl into ions is balanced almost exactly by the energy released by water molecules attracting themselves to the sodium ions.

**Experiment 5.2.** To determine the heat of solution of anhydrous and hydrated calcium chloride.

**Apparatus.** As given in Experiment 5.1.

**Chemical.** Anhydrous and hydrated calcium chloride.

**Procedure.** Set up the apparatus shown in Fig. 5.2. Pour 50 ml of distilled water into the beaker. After sometime take its temperature when steady. Add a weighed mass of about 1 g of anhydrous calcium chloride. Stir the solution well and read the maximum temperature that the solution attains.

Repeat the experiment with a weighed mass of about 2 g of hydrated calcium chloride.

**Observations.** Initial temperature of water$=t_1$°C

Final temperature of water or (solution)$=t_2$°C

Mass of anhydrous calcium chloride used $=1\text{ g}=w_1\text{g}$

**Calculations.** Total mass of solution$=(50+w_1)\ g$

Assuming that, as for water, 4·18 J are required to raise the temperature of 1 g of solution by 1°C.

Let the water equivalent of calorimeter be $W$.

Rise in temperature $=(t_2-t_1)=t$°C

Heat gained by calorimeter$=W\times t$ J/deg.

Heat gained by solution $=(50+w_1)\times t\times 4{\cdot}18$ J

Total heat change of the solution

$$Q=[(W\times t)+(50+w_1)\times t\times 4{\cdot}18)]\ \text{J}$$

$$=x\ \text{J}$$

Heat liberated by 1 mole of (111 g) of $CaCl_2$

$$=\frac{x\times 111}{w_1} \text{ g or 71 kJ mol}^{-1} \text{ (experimental value)}$$

**Result.** $\Delta H$ (of solution)$=-71$ kJ mol$^{-1}$

**Remarks. 1.** The negative heat of solution for the anhydrous calcium chloride shows that the energy of hydration for $Ca^{2+}$ ions exceeds the energy used in separating the calcium and chloride ions.

2. For the hydrated calcium chloride you will find that the temperature will fall because the ions in the salt already exist in the hydrated state. Therefore when the salt dissolves the energy is required to separate the ions. Thus the temperature falls. The dissolution of hydrated calcium chloride is an endothermic process.

## ORAL QUESTIONS AND ANSWERS

**Q. 5.1.** What do you understand by calorific value of a substance ?

**Ans.** It is defined as the amount of heat produced in calories when one gram of the substance is completely burnt. It may also be defined as the amount of heat produced in kilocalories when one kilogram of the substance is completely burnt.

**Q. 5.2.** What is the importance of the knowledge of calorific value ?

**Ans.** The knowledge of calorific value is very helpful in rating different fuels. For example, calorific value of wood is 4000 calories or 4 kcal per gram while that of charcoal is 8000 calories or 8 k cal per gram. Thus, charcoal is a better fuel as compared to wood.

**Q. 5.3.** Define calorie.

**Ans.** The amount of heat required to raise the temperature of 1 gram of water through 1°C (14·5 to 15·5°C) is known as calorie.

**Q. 5.4.** Which of the followings is the best fuel and why ?

Wood, kerosene oil, burshane gas and charcoal

**Ans.** Burshane gas is the best fuel, as its calorific value is higher than that of the three other fuels.

**Q. 5.5.** What are endothermic reactions ?

**Ans.** The reactions which proceed with the absorption of heat are termed as endothermic reactions. Example :

$$2NO+O_2 \longrightarrow 2NO_2-\text{heat}$$

In this reaction, heat is supplied to the system, hence $\Delta H$ is +ve.

**Q. 5.6.** What are exothermic reactions ?

**Ans.** The reactions which proceed with the evolution of heat are termed as exothermic reactions. Example :

$$N_2+3H_2 \longrightarrow 2NH_3+\text{heat}$$

In this reaction, heat is lost by the system, hence $\Delta H$ is $-$ve.

**Q. 5.7.** Define chemical energy.

**Ans.** The energy stored in chemical substances is called chemical energy.

**Q. 5 8.** Give the various energy units.

**Ans.** Eenergy is measured in joules (symbol J).

A joule is defined as the quantity of energy transferred when a force of 1 Newton acts through a distance of 1 meter. A joule is also equal to the energy change when 1 coulomb of electricity flows through a potential difference of 1 volt or when 1 watt of electrical power flows for 1 second. Heat energy is also measured in calories. A calorie is the quantity of heat required to raise the temperature of 1 g of water by 1°C (1 kelvin). 4·18 joules are needed to raise the temperature of 1 g of water by 1°C, hence, 4·18 joules are equal to 1 calorie. The joule is such a small amount of energy that it is often convenient to use kilojoules (symbol kJ ; 1000 J=1 kJ)

**Q. 5.9.** Define heat capacity and molar heat capacity.

**Ans.** See Section 5.2.

**Q. 5.10.** Define the following :
mole, molar mass and molarity.

**Ans.** **Mole**. A mole is the amount of substance that contains as many elementary entities (*e.g.* atoms, molecules, empirical formula units) as there are atoms in 0·012 kg (12 g) of C-12.

$$1 \text{ mole}=6{\cdot}022\times 10^{23} \text{ entities.}$$

**Molar mass.** It is the mass of 1 mole of a substance.

**Molarity.** It is the concentration of a solute in solution expressed in moles per litre ($M=\text{mol } L^{-1}$).

**Q. 5.11.** What is a calorimeter ?

**Ans.** It is a device used to measure the quantity of heat absorbed or evolved during a chemical reaction or a physical change.

**Q. 5.12.** Why are metallic calorimeters not used in thermochemical experiments ?

**Ans.** Metallic calorimeters are not used as the chemical substances used in the experiments may react with them.

**Q. 5.13.** Define heat of neutralization.

**Ans.** See Section 5.3.

**Q. 5.14.** Define the term 'water equivalent of a calorimeter.'

**Ans.** Water equivalent of a calorimeter may be defined as the amount of heat required to raise the temperature of calorimeter through 1°C or 1 kelvin.

**Q. 5.15.** Why is the heat of neutralization for weak acid or alkali, different from strong acid or alkali ?

**Ans.** This is because weak acids or alkalis are only slightly ionized in aqueous solution and energy is used up as they ionize before neutralization. Although the numerical value is generally less than $-57{\cdot}3$ kJ (for strong acid and alkali), in some cases it can be greater.

**Q. 5.16.** Give a few examples of weak acids or alkalis where the heat of neutralization is greater/less than $-57{\cdot}3$ kJ.

**Ans.**

1. $NH_4OH(aq)+HCl(aq) \longrightarrow NH_4^+(aq)+Cl^-(aq)+H_2O(l)$
$$\Delta H(298\ K)=-51{\cdot}4\ kJ\ mol^{-1}$$
2. $CH_3COOH(aq)+NaOH(aq)$
$$\longrightarrow CH_3COO^-(aq)+Na^+(aq)+H_2O(l)$$
$$\Delta H(298\ K)=-55{\cdot}2\ kJ\ mol^{-1}$$
3. $HF(aq)+NaOH(aq) \longrightarrow NaF(aq)+H_2O(l)$
$$\Delta H(298\ K)=-68{\cdot}6\ kJ\ mol^{-1}$$

**Q. 5.17.** Define heat of solution ?

**Ans.** See section 5.4.

**Q. 5.18.** 'Water is considered to be a good solvent'. Comment.

**Ans.** As water molecules have large dipoles, strong interactions are possible between the polar water molecules and solute ions. These strong interactions result in a high negative heat of solvation, which makes water a good solvent. Non-polar solvents such as hydro-carbons, do not dissolve ionic substances because there is no negative heat of solvation to compensate for the positive lattice dissociation enthalpy.

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## UNIT 6

# Electrochemical Cells and Electroplating

### 6.1. Introduction

Electrochemistry is that branch of chemistry which deals with the relationship between chemical energy and electrical energy and how one is converted into another. Electrochemistry may be subdivided in two general areas which are essentially the inverse of each other although governed by common principles. The first involves the study of the methods, principles and reactions used in transforming electrical energy into some specific chemical changes. The second involves the study of methods, principles and reactions used in transforming chemical changes into electrical energy. The first, of these two, is called 'electrolysis' and the second is named as 'electromotive chemistry'. The cells used for electrolysis are called 'electrolytic cells' while cells used in electromotive chemistry are called 'electrochemical cells' (galvanic or voltaic cells). Primarily both electrolytic or electrochemical cells involve transport of electrical charge through chemical systems. For many chemical reactions the fundamental change that occurs can be described in terms of the transfer of electrons, *i.e.*, oxidation-reduction.

To understand this, consider a reaction between a piece of zinc and a solution of copper sulphate. The zinc soon becomes coated with a reddish deposit of metallic copper, and the blue colour of the solution begins to fade. If enough zinc is present and enough time allowed, the solution eventually becomes colourless. These changes result from a reaction in which electrons are transferred from zinc to copper, each $Cu^{2+}$ ion deposited as metallic copper takes two electrons from a zinc atom which dissolves as zinc ion.

$$\underset{\text{(Slivery)}}{Zn(s)} + \underset{\text{(Blue)}}{Cu^{2+}(aq)} \longrightarrow \underset{\text{(Colourless)}}{Zn^{2+}(aq)} + \underset{\text{(Red)}}{Cu(s)}$$

Here zinc is oxidized to $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$ is reduced to copper metal. This reaction can be used as the basis of an electrochemical cell to produce an electric current.

### 6.2. Cell Potential

The electric current produced by an electrochemical cell (Fig. 6.1) is the result of electrons being pushed out of the zinc electrode around the external circuit to the copper electrode where they are used up. When an electric current flows between two electrodes, we say that there is a potential difference between the two electrodes. The current flows from the higher potential to the lower potential. This potential difference is measured in volts and is often called the voltage of the cell. The potential between the electrodes of an electrochemical cell is called the cell potential, $E_{cell}$. If no current is taken from the cell the potential difference between the electrodes will be maximum and will be equal to the potential of the cell (emf). The cell potential depends upon the concentrations of the solutions in the cell, the temperature, and the partial pressures of any gases that might be involved in the cell reactions. When the effective concentrations for the solutions are $1ML^{-1}$, all partial pressures of gases are 1 atm and the temperature is 298 K, the cell potential (emf) is called the standard emf (cell potential) of the cell and is given the symbol $E°_{cell}$.

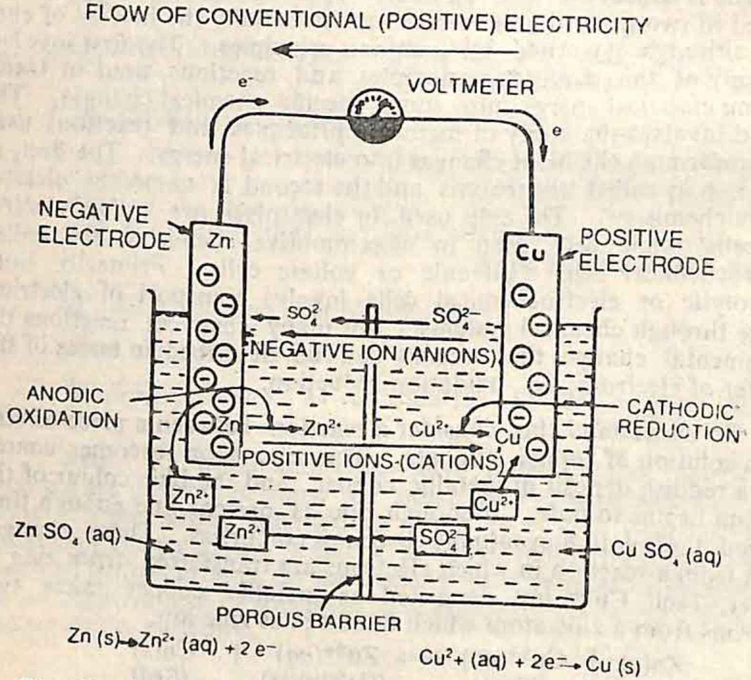


Fig. 6.1. A galvanic cell with porous diaphragm or portion to prevent the mixing of two electrolytes contained in the cell. Atoms of the zinc metal dissolve as positive ions, leaving a build up of electrons on the metal. Hence the zinc metal will become negatively charged. The copper strip becomes positively charged as the $Cu^{2+}$ ions (present in solution take electrons from it.

Differences in electrical potential between pairs of electrodes can be determined with precision. Single electrode potentials, on the other hand, cannot be determined at all because for a couple in isolation a reversible equilibrium exists. However, if an electrode with some arbitrary value is chosen as reference electrode (standard), then precise relative potentials can be determined for other electrodes by comparison with this reference.

The emf of any cell is the algebraic sum of the oxidation standard potential of the species being oxidized in the cell reaction and the standard reduction potential of the species being reduced. Hence, the emf of a galvanic cell, $E_{cell}$ can be readily found from the reduction half-cell potentials using the relationship (usual notations for representing a cell has been used).

$$E_{cell}=E_{right}-E_{left}=E\text{Cu}-E\text{Zn}$$

By convention, the emf, E, is taken to act from left to right through the cell. A positive emf indicates that electrons are flowing from left to right through the external circuit (in Fig. 6.1, from Zn to Cu). The flow of conventional electricity (positive electricity) is therefore from right to left through the external circuit (from Cu to Zn in Fig. 6.1)

## 6.3. Electrolysis

Electricity involves flow of electrons through metals and movement of ions through solutions. Some substances dissolve in water and split into ions. These substances are called *electrolytes*. Ions are charged particles and possess certain electrical properties. The positively charged ions are known as *cations* and negatively charged ions are known as *anions*. When electric current is passed through an acidified solution of copper (II) chloride, $CuCl_2$, copper ions ($Cu^{2+}$) are attracted towards one electrode (cathode) and chloride

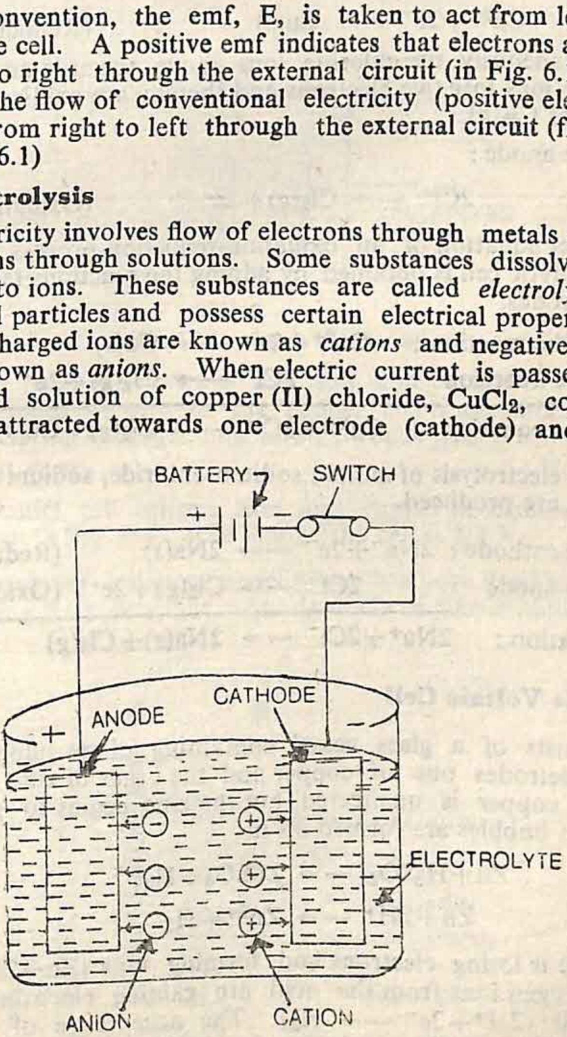


Fig. 6.2. An electrolytic cell. Electrolysis of cupric chloride solution.

ions ($Cl^-$) are attracted towards the other (anode). The process in which a chemical change is caused by passing an electric current through an electrolyte is known as *electrolysis*. The cell in which electrolysis is carried out is known as an *electrolytic cell*. The reactions that occur at the electrodes are oxidation-reduction reactions. In the electrolysis of $CuCl_2(aq)$ (Fig. 6.2), copper deposits at the cathode because the $Cu^{2+}$ ions attract electrons and are reduced.

At the cathode :

$$Cu^{2+}+2e^- \longrightarrow Cu(s) \qquad \text{(Reduction)}$$

Simultaneously, the chloride ions move towards anode where two chloride ions lose two electrons and thereby are oxidized forming a molecule of $Cl_2(g)$.

At the anode :

$$2Cl^- \longrightarrow Cl_2(g)+2e^- \qquad \text{(Oxidation)}$$

The net equation of an oxidation-reduction process occurring in an electrolytic cell is obtained by adding the reactions taking place at the electrodes.

$$\begin{array}{lrl} \text{Cathodic reaction :} & Cu^{2+}+2e^- & \longrightarrow Cu(s) \\ \text{Anodic reaction :} & 2Cl^- & \longrightarrow Cl_2(g)+2e^- \\ \hline \text{The net equation :} & Cu^{2+}+2Cl^- & \longrightarrow Cl_2(g)+Cu(s) \end{array}$$

In the electrolysis of molten sodium chloride, sodium metal and chlorine gas are produced.

$$\begin{array}{lrll} \text{At the cathode :} & 2Na^-+2e^- & \longrightarrow 2Na(s) & \text{(Reduction)} \\ \text{At the anode :} & 2Cl^- & \longrightarrow Cl_2(g)+2e^- & \text{(Oxidation)} \\ \hline \text{The net equation :} & 2Na^++2Cl^- & \longrightarrow 2Na(s)+Cl_2(g) & \end{array}$$

## 6.4. Simple Voltaic Cell

It consists of a glass vessel containing dilute sulphuric acid, and two electrodes one of copper and the other of zinc immersed in it. The copper is unaffected but the zinc begins to react and hydrogen gas bubbles are formed on it.

$$Zn+H_2SO_4 \longrightarrow ZnSO_4+H_2$$

or

$$Zn+2H^+ \longrightarrow Zn^{2+}+H_2$$

Here the zinc is losing electrons and forming ions ($Zn \rightarrow Zn^{2+}+2e^-$) and the hydrogen ions from the acid are gaining electrons to form hydrogen gas ($2H^++2e^- \longrightarrow H_2$). The acceptance of electrons (from Zn) by $H^+$ ions (from acid) to give hydrogen gas is known as a local action, and can be supressed by rubbing a little mercury on the zinc plate.

If now the treated zinc plate and the copper plate are connected by a wire through a voltmeter, as in Fig. 6.3, the voltmeter registers a voltage, the zinc begins to react and bubbles of hydrogen begin to accumulate on the copper electrode.

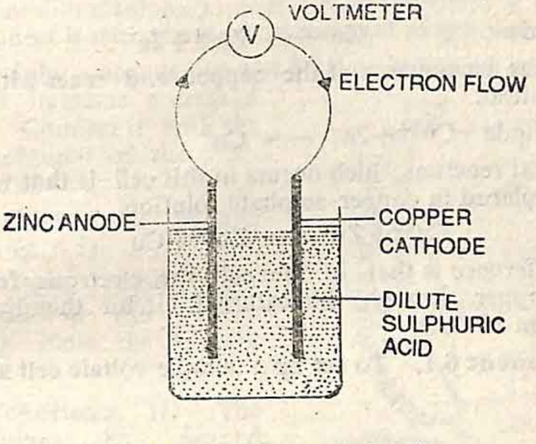


Fig. 6.3. A simple voltaic cell.

This is because electrons are now able to flow from the zinc electrode through the wire to the copper electrode, where they are used in converting hydrogen ions into hydrogen gas.

### 6.5. Daniel Cell

The Daniel cell utilizes zinc and copper in solutions of their ions as shown in Fig. 6.4. The emf of the cell is 1·1 V.

It consists of a copper vessel which has been divided into two parts by a circular porous pot. Anode made of zinc is immersed into

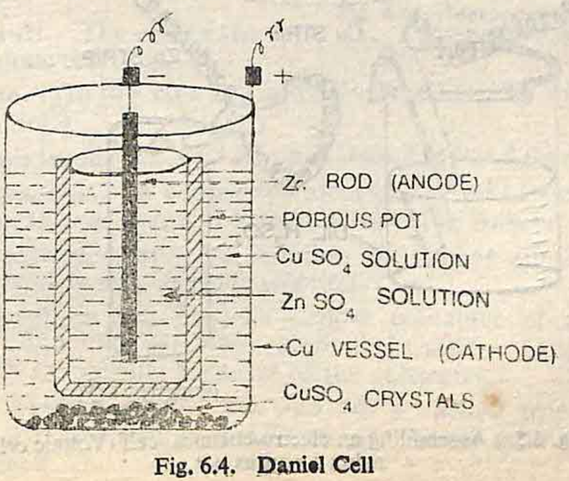


Fig. 6.4. **Daniel Cell**

$ZnSO_4$ contained in a porous pot. The pot is surrounded by copper. sulphate solution (Fig. 6.4). Copper vessel works as cathode. Zinc has a greater tendency to lose electrons than copper. If the electrodes are connected together through a voltmeter then electrons released by zinc atoms flow through the wire to the copper and zinc passes into solution as ions.

At anode $Zn \longrightarrow Zn^{2+} + 2e^-$

Electrons accumulate on the copper and react with $Cu^{2+}$ ions from the solution.

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$

The total reaction which occurs in this cell is that which occurs when zinc is placed in copper sulphate solution.

$$Cu^{2+} + Zn \longrightarrow Zn^{2+} + Cu$$

The difference is that in the cell the electrons from the zinc reach the copper through the external circuit thereby causing an electric current to flow.

**Experiment 6.1.** To set up a simple voltaic cell and measure its emf.

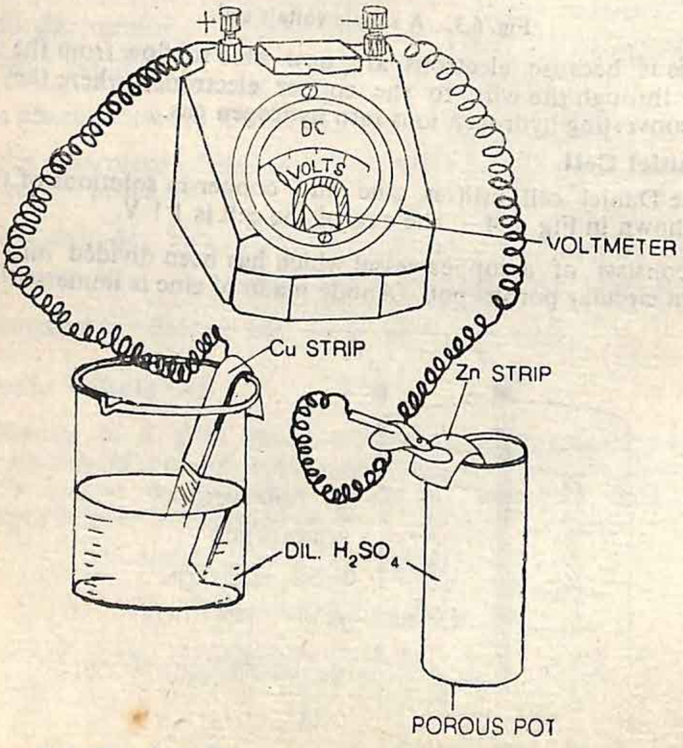


Fig. 6.5. Assembling an electro-chemical cell (Voltaic cell) using a porous pot.

**Apparatus.** A beaker of 250 ml capacity, a porous pot, an amalgamated zinc strip or rod, a copper strip or rod, connecting wires, a voltmeter, etc.

**Chemical.** Dilute sulphuric acid.

**Procedure.** (*i*) Take a beaker of 250 ml capacity and fill it with 100 ml dilute sulphuric acid. Now immerse a strip of copper in it. Connect it with the positive terminal of the voltmeter.

(*ii*) Take a porous pot and fill it with 100 ml of sulphuric acid. Now immerse a strip of zinc in it. Connect it with the negative terminal of the voltmeter.

(*iii*) Note the voltage reading (Fig. 6.5).

(*iv*) Now place the porous pot in the beaker (Fig. 6.6). Note the voltage reading.

**Precautions.** (*i*) The strips should be cleaned properly by rubbing them with sand paper before dipping into the acid (or electrolytes.)

(*ii*) Porous pot should be washed thoroughly by throwing water into it by force.

(*iii*) The ends of the connecting wires should be cleaned by sand paper.

**Result**. The emf of the simple voltaic cell is ......V.

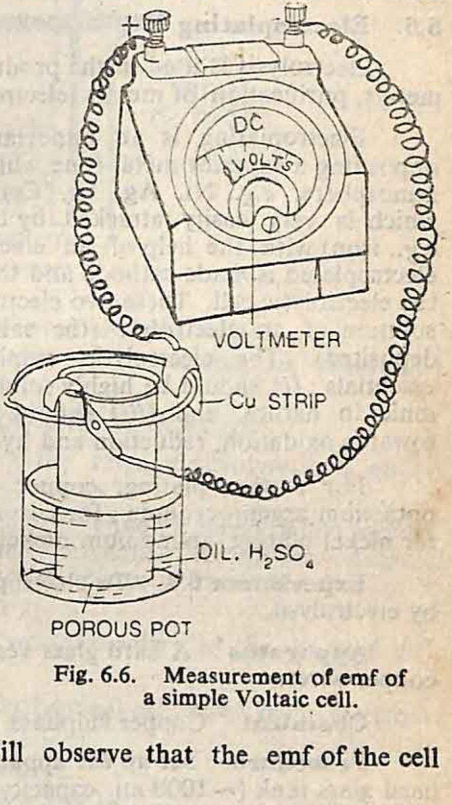


Fig. 6.6. Measurement of emf of a simple Voltaic cell.

**Note**. (In this case you will observe that the emf of the cell falls with time).

**Experiment 6.2**. To set up a Daniel cell and measure its emf.

**Apparatus**. A copper container of 250 ml capacity, a porous pot, a zinc strip or rod, a voltmeter, connecting wires, etc.

**Chemical**. Saturated solution of copper sulphate, copper sulphate crystals zinc sulphate solution.

**Procedure.** (*i*) Take a copper container of about 250 ml capacity. Fill it with saturated solution of $CuSO_4$. Connect the container with the positive terminal of the voltmeter.

(*ii*) Take a porous pot and fill it with a solution of zinc sulphate. Put zinc strip in it. Connect it with the negative terminal of the voltmeter.

(*iii*) Note the voltage reading at this stage.

(*iv*) Now put the porous pot with its contents in the copper vessel. Note the voltage reading.

**Precautions.** Same as in Experiment 6.1.

**Result.** The emf of the Daniel cell is ...... V.

**Note.** (In this case you will observe that the emf of the cell remains constant).

## 6.6. Electroplating

Electrolysis is used in the production of certain metals and non-metals, purification of metals (electrorefining) and in electroplating.

Electroplating is an important techinque and is the art of depositing a superior metal (one which is not easily attacked by the atmosphere, *e.g.*, Ni, Ag, Sn, Cr) over another baser metal (one which is very easily attacked by the atmosphere and gets rusted, *e.g.*, iron) with the help of an electric current. The object to be electroplated is made cathode and the plating metal is made anode in the electrolytic cell. These two electrodes are dipped into the aqueous solution of an electrolyte (the salt solution of the metal to be deposited). The electrolytic employed should fulfil the following essentials : (*i*) should be highly soluble in water, (*ii*) should be highly ionic in nature, and (*iii*) should be easily available and stable towards oxidation, reduction and hydrolysis.

For copper plating, copper sulphate ; for silver plating, potassium argentocyanide ; for chrome plating, dichromic acid, and for nickel plating, ammonium nickel sulphate are used.

**Experiment 6.3.** To electrophate a strip of iron with copper by electrolysis.

**Apparatus.** A hard glass vessel, a copper strip, an iron strip, copper wires.

**Chemical.** Copper sulphate, distilled water.

**Procedure.** Set up the apparatus as shown in Fig. 6.7. In a hard glass tank ($\sim$1000 ml capacity), take 800 ml of 10% aqueous solution of copper sulphate solution. Suspend the electrodes (copper strip and iron strip) in the solution contained in the tank with a support. Connect the electrodes through connecting wires of copper to the mains through a variable resistance box as shown in Fig. 6.7. Pass the current between the electrodes. You will observe, that as the operation proceeds anodic copper dissolves in solution and gets deposited on the iron strip (cathode). After sometime say 30 minutes stop the supply and take out the cathode. A bright uniform layer of metallic copper will be seen on the iron strip.

**Precautions.** (*i*) The copper strip and the iron object should be thoroughly cleaned by rubbing them with sand paper.

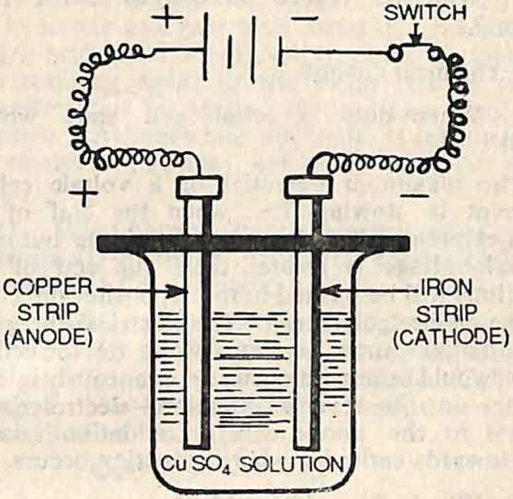


Fig. 6.7. Electroplating of iron object with copper.

(*ii*) Take other usual percautions while handling the electrical equipments.

## ORAL QUESTIONS AND ANSWERS

**Q. 6.1.** What is meant by the term electrolyte, and what three classes of compounds are electrolytes ?

**Ans.** Those compounds which conduct electricitry when they are dissolved in water or melted, are called electrolytes. Acids, alkalis and salts are the most important groups of electrolytes.

**Q. 6.2.** What is electrolysis ?

**Ans.** The decomposition of one electrolyte by the passage of electric current is electrolysis.

**Q. 6.3.** How does an electrochemical cell differ from electrolytic cell ?

**Ans.** See Section 6.1 of this unit.

**Q. 6.4.** What are cations and anions ?

**Ans.** The ions moving towards the negative electrode (cathode) are called cations and these moving towards the positive electrode (anode) are called anions.

**Q. 6.5.** Define electrode, cathode and anode.

**Ans.** *Electrode.* It is a metallic strip, sheet or rod used for carrying electric current.

*Cathode.* It is an electrode which is connected to the positive terminal of the battery. Reduction occurs at the cathode.

*Anode.* It is an electrode which is connected to the negative terminal of the battery. Oxidation occurs at the anode.

**Q. 6.6.** Will you regard electrolysis as a chemical or physical change ?

**Ans.** A chemical change.

**Q. 6.7.** When does a voltaic cell start working as an electrolytic cell ?

**Ans.** The maximum potential of a voltaic cell is observed when no current is flowing, *i.e.*, when the emf of the cell is opposed by an external voltage of equal magnitude but opposite sign. If this external voltage is greater than the emf of the cell, the electrode reactions will be pushed in the opposite direction and the cell will become an electrolytic cell. The electrical energy supplied by the external potential source performs work on the cell, and the cell reaction, which would otherwise occur spontaneously in one direction, now takes place in the reverse direction—electrolysis results, *i.e.* anions migrate to the anode, where oxidation takes place and cations move towards cathode, where reduction occurs.

**Q. 6.8.** Why is the relationship between anode and cathode and positive and negative electrodes is different in the electrochemical and electrolytic cell ?

**Ans.** In the Daniel cell (electrochemical cell), oxidation occurs at the zinc electrode and also from this electrons leave the voltaic cell. Hence, this electrode is defined as the anode. It is at the copper electrode that electrons enter the cell and a reduction takes place. Hence, this electrode is defined as the cathode. Electrons are negatively charged particles and so they flow from the negative to positive electrode through the wire connecting them. Hence, in the electrochemical cell, the zinc anode is the negative electrode and the copper cathode is the positive electrode.

In the electrolytic cell, the electrode where the electrons enter the cell and a reduction takes place is again the cathode (by definition), and the electrode where electrons leaves the cell and an oxidation takes place is again the anode (by definition). But as the electrons are being fed into the cell from an external source (battery) the electrode where the electrons enter the cell will be more negative than the electrode where the electrons leave, *i.e.*, the cathode will be the negative electrode and the anode the positive electrode.

**Q. 6.9.** Why is the electrolysis of pure water not feasible ? What purpose does added $H_2SO_4$ or $Na_2SO_4$ serve ?

**Ans.** Pure water is not a very good electrolyte. It conducts electricity to a very small extent. In the presence of $H_2SO_4$ or $Na_2SO_4$, water starts behaving as a better electrolyte and along with $H_2SO_4$ and $Na_2SO_4$ dissociates into $H^+$ and $OH^-$ ions.

**Q. 6.10.** Why does the emf of a simple voltaic cell fall with time ? How will you overcome this problem ?

**Ans.** In a simple voltaic cell as illustrated in Fig. 6.3, the voltage generated drops quickly as hydrogen bubbles cover the copper plate. This is known as polarisation, and if the cell is to continue working the hydrogen gas, generated from the reaction of zinc with dilute sulphuric acid, must be removed by either shaking the electrode or adding an oxidizing agent to the electrolyte in the cell so that some other preferential electrode reaction takes place and hydrogen gas is not formed. At times zinc electrode is substituted by amalgamated zinc electrode. It does not react with dil $H_2SO_4$ to give hydrogen gas.

**Q. 6.11.** What happens in the electrolysis of copper sulphate solution between (*i*) platinum plates (*ii*) copper cathode and platinum anode, and (*iii*) Copper plates ?

**Ans.** (*i*) $CuSO_4$ yields $Cu^{2+}$ and $SO_4^{2-}$ Ions. Water yields a small number of $OH^-$ and $H^+$ ions. When the electric current is supplied $Cu^{2+}$ and $H^+$ ions move to the cathode. $Cu^{2+}$ ions are more readily disharged than $H^+$ ions (electrochemical series) and metallic copper is deposited on the cathode

$$Cu^{2+}+2e^- \longrightarrow Cu$$

At the anode the ions $OH^-$ are discharged yielding water and oxygen.

(*ii*) Same reactions take place as given in (*i*).

(*iii*) Here the same reactions take place at the cathode. At the anode neither $OH^-$ nor $SO_4^{2-}$ are discharged. Instead the anode gains its electrons by conversion of copper of the anode into ions which go into solution :

$$Cu \longrightarrow Cu^{2+}+2e^- \text{ (electrons are left on the anode)}$$

Here the cathode grows at the expense of the anode. This fact has been made the basis of electrolytic purification of copper.

**Q. 6.12.** Define cell potential, emf and standard cell potential.

**Ans.** See Section 6.2.

**Q. 6.13.** What happens when a metal plate(M) is immersed in a solution containing the ions $M^{n+}$

**Ans.** There are three possibilities when a metal plate is immersed in a solution containing the ion $M^{n+}$

(*i*) A metal ion $M^{n+}$ may come in the contact of the electrode and experience no change.

(*ii*) A metal ion $M^{n+}$ may come in the contact of the electrode, accept *n* electrons and be reduced to a metal atom M.

(*iii*) A metal atom on the electrode M may oxidize and thereby lose *n* electrons to the electrode and enter the solution as $M^{n+}$.

When equilibrium is attained, a small difference in electrical potential exists between the metal electrode and the solution. A metal with a strong tendency of losing electrons, imparts $M^{n+}$ ions to solution resulting in a fractional increase in the number of metal ions, $M^{n+}$ in solution and a fractional increase in the number of electrons on the electrode. As a result, the electrode develops a small negative potential with respect to the solution.

$$M(s) \xrightarrow[\text{Reduction}]{\text{Oxidation}} M^{n+}(aq) + ne^-$$

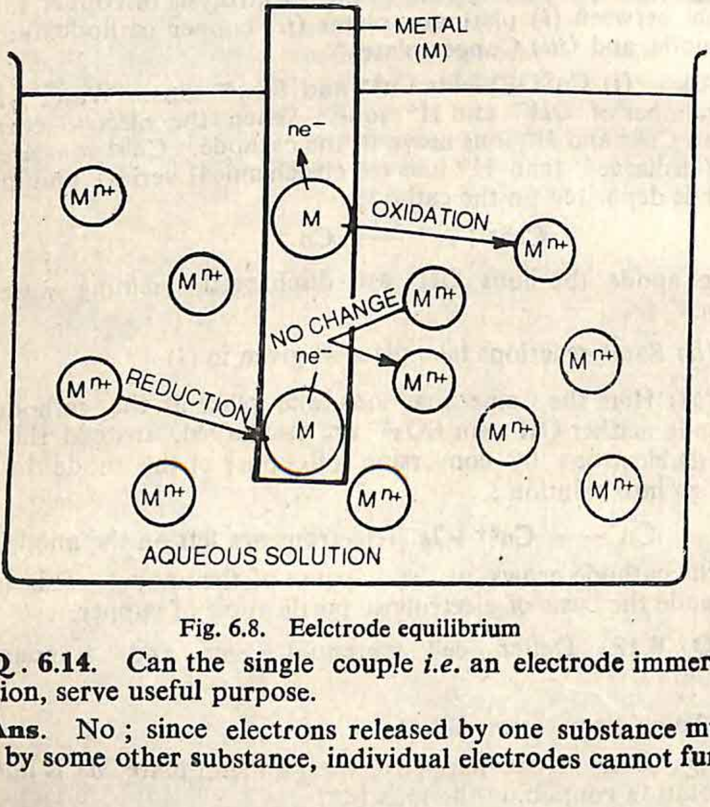


Fig. 6.8. Eelctrode equilibrium

**Q. 6.14.** Can the single couple *i.e.* an electrode immersed in a solution, serve useful purpose.

**Ans.** No ; since electrons released by one substance must be gained by some other substance, individual electrodes cannot function alone.

☐ ☐

# UNIT 7

## Qualitative Analysis of Inorganic Salts—Identification of Gases

### 7.1. Introduction

In qualitative analysis, we learn to make observations accurately and to interpret them logically. This is, perhaps, the single most important thing we learn in the entire educational curriculum. We shall see the effects of various kinds of equilibria encountered in

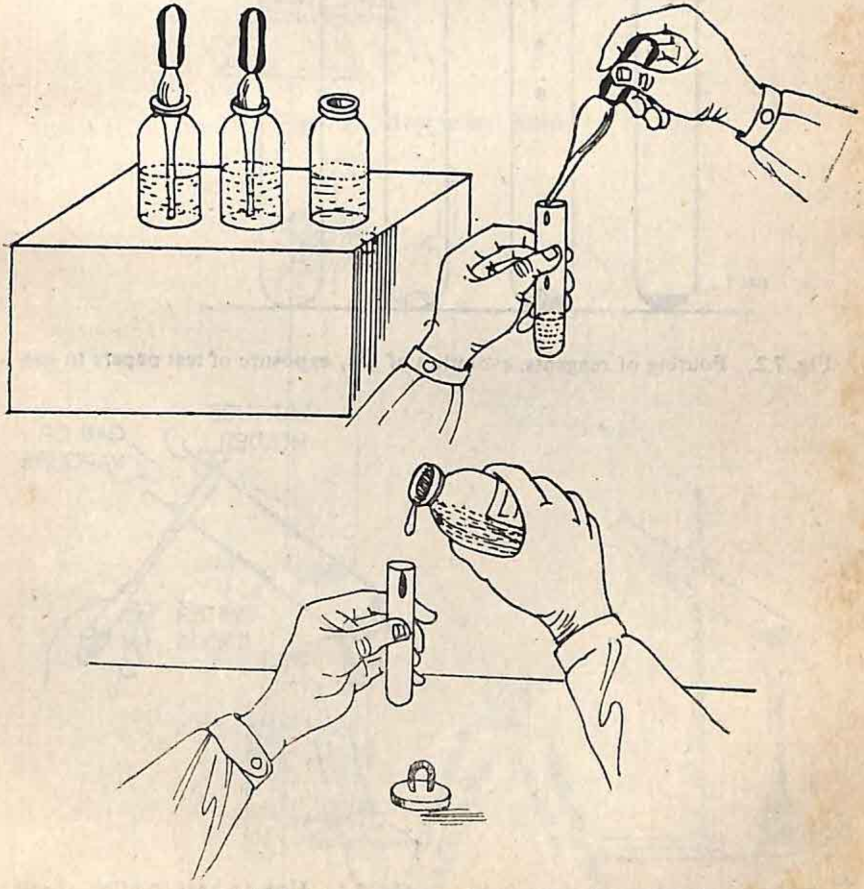


Fig. 7.1. Pouring of reagents

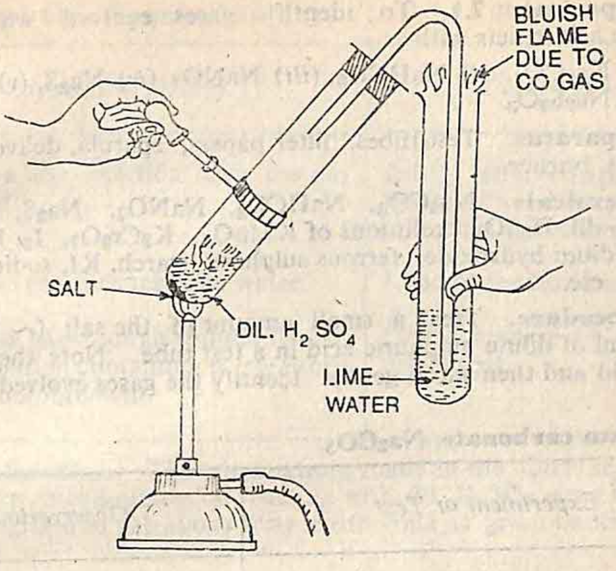
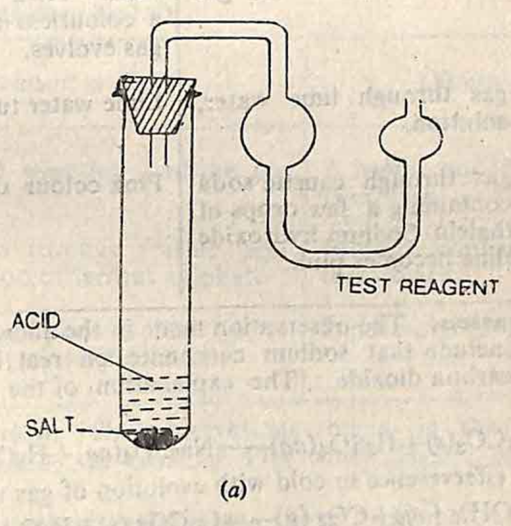


Fig. 7.5. How to test gases



(a)

(b)

Fig. 7.6. How to test gases

several types of chemical reactions. We shall observe (*i*) evolution of gases, (*ii*) the precipitation of compounds, (*iii*) the dissolution of precipitates/insoluble compounds by complex formation, etc.

Qualitative analysis is concerned with the identification of ions present in the given salts. Some of the salts (or anions) react with strong acids to liberate gases which in turn are identified by chemical tests. On the basis of this we are able to gather some informations about anions which may be present. Handling of the salt, reagent, etc. is shown through various figures.

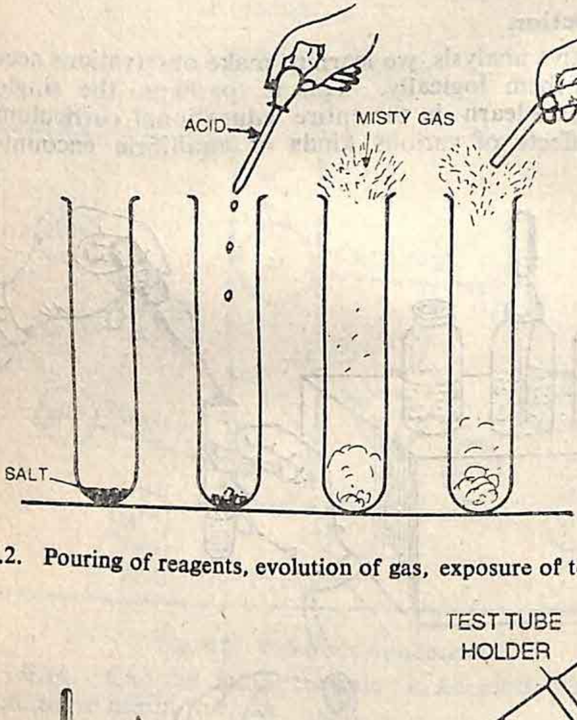


Fig. 7.2. Pouring of reagents, evolution of gas, exposure of test papers to gas

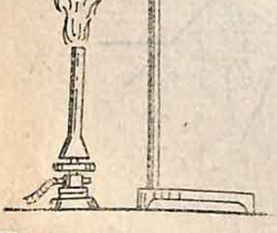


Fig. 7.3. Position of the test tube while being heated

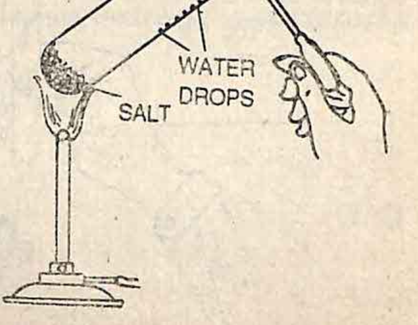


Fig. 7.4. How to heat solution or salt

**Experiment 7.1**. To identify gases evolved when dilute sulphuric acid reacts with

(*i*) $Na_2CO_3$, (*ii*) $NaHCO_3$, (*iii*) $NaNO_2$, (*iv*) $Na_2S$, (*v*) $Na_2SO_3$, and (*vi*) $Na_2S_2O_3$

**Apparatus**. Test tubes, filter papers, spatula, delivery tubes, glass rods, burner.

**Chemicals**. $Na_2CO_3$, $NaHCO_3$, $NaNO_2$, $Na_2S$, $Na_2SO_3$, $Na_2S_2O_3$, dil. $H_2SO_4$, solutions of $KMnO_4$, $K_2Cr_2O_7$, $I_2$, $Br_2$, lime water, sodium hydroxide, ferrous sulphate, starch, KI, sodium nitroprusside, etc.

**Procedure**. Treat a small amount of the salt (~ 2g) with about 3 ml of dilute sulphuric acid in a test tube. Note the reaction in the cold and then warm gently. Identify the gases evolved as given under :

(*i*) **Sodium carbonate, $Na_2CO_3$.**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | With brisk effervesence, a colourless and odourless gas evolves. |
| 2. Pass the gas through lime water, $Ca(OH)_2$ solution. | Lime water turns milky. |
| 3. Pass the gas through caustic soda solution containing a few drops of phenolphthalein. Sodium hydroxide being alkaline becomes pink. | Pink colour disappears. |

**Explanation.** The observation made in the above experiments lead us to conclude that sodium carbonate on reacting with dil. $H_2SO_4$ gives carbon dioxide. The explanation of the above test is given below ;

1. $Na_2CO_3(s)+H_2SO_4(aq)\longrightarrow Na_2SO_4(aq)+H_2O(l)+CO_2(g)$

A brisk effervesence in cold with evolution of gas takes place.

2. $\underset{\text{Lime water}}{Ca(OH)_2}\ (aq)+CO_2\ (g)\longrightarrow \underset{\text{(Insoluble)}}{CaCO_3\ (s)}+H_2O\ (l)$

Lime water turns milky due to the formation of $CaCO_3\ (s)$

3. $\underset{\text{Phenolphthalein}}{NaOH\ (aq)}+CO_2\ (g) \longrightarrow NaHCO_3(aq)$

Pink colour of the solution discharges due to the conversion of NaOH into $NaHCO_3$ which gives colourless solution with phenolphthlein. Carbon dioxide is acidic in nature as it neutralizes alkalis, like NaOH and $Ca(OH)_2$.

(*ii*) **Sodium bicarbonate, $NaHCO_3$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | Brisk effervesence takes place with the evolution of colourless and odourless gas. |
| 2. Pass the gas through lime water. | Lime water turns milky. |
| 3. Pass the gas through sodium hydroxide solution containing a few drops of phenolphthalein. | Pink colour of the solution discharges. |

**Explanation**. The observations made in the above tests show that sodium bicarbonate on reacting with dil. $H_2SO_4$ gives $CO_2$ gas. The explanation of the above tests is the same as given under sodium carbonate.

$$2NaHCO_3(aq)+H_2SO_4(aq) \longrightarrow Na_2SO_4(aq)+2H_2O(l)+2CO_2(g)$$

(*iii*) **Sodium nitrite, $NaNO_2$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A brown and pungent gas is evolved. |
| 2. Pass the gas through freshly prepared solution of ferrous sulphate. | Ferrous sulphate solution turns black. |
| 3. Expose a small piece of filter paper dipped in starch+KI solution. | Paper turns blue. |

**Explanation**. The observations made in the above tests reveal that $NaNO_2$ on reacting with dilute $H_2SO_4$ gives NO and $NO_2$.

The observations made in the above tests can be explained as give below :

1. $$2NaNO_2(s)+H_2SO_4(aq) \longrightarrow Na_2SO_4(aq)+NO(g)+NO_2(g)+H_2O(l)$$

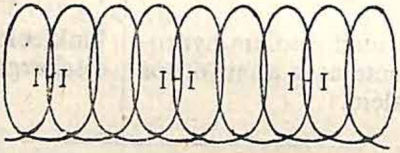
You may recall that NO reacts with oxygen very rapidly to form brown gas.

2. $$FeSO_4+NO \longrightarrow \underset{\text{(Black Coloure)}}{[Fe(NO)^-]\,SO_4 \text{ or } [Fe\,NO(H_2O)_5]SO_4}$$

In acidic solution, $NO_2^-$ ions oxidize $Fe^{2+}$ ion and are reduced to nitric oxide, NO. An excess of $Fe^{2+}$ ions is added to ensure that the reaction goes to completion.

$$NO_2^- + Fe^{2+} + 2H^+ \longrightarrow Fe^{3+} + NO + H_2O$$

3. In acidic solution $NO_2^-$ ions oxidize $I^-$ ions and are reduced to nitric oxide, NO. The oxidized product, *i.e.*, $I_2$ reacts with starch and form a deep blue coloured product. It is used as a sensitive test for iodine. The blue colour disappears on heating and is due to absorption of iodine molecules within the helical starch molecules.



Helical starch molecule
$(C_6H_{10}O_5)_n$

$NO_2$ acts as an oxidizing agent.

$$NO_2 + 2I^- + H_2O \longrightarrow NO + I_2 + 2OH^-$$

(*iv*) **Sodium sulphide, $Na_2S$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A colourless gas with smell of rotten eggs is evolved. |
| 2. Pass the gas through acidified solution of lead acetate. | Solution of lead acetate turns black. |
| 3. Introduce a burning splinter into the test tube full of gas. | Gas starts burning with a pale blue flame and the splinter extinguishes. Yellow particles of sulphur appear on the walls of the jar. |
| 4. Pass the gas through acidified $KMnO_4$ (dilute) solution for long. | It is decolourized. |
| 5. Pass the gas through bromine water solution. | It is decolourized. |
| 6. Pass the gas through sodium nitroprusside solution to which a few drops of alkali has been added. | Turns red-violet in colour. |

**Explanation**. The observations made in the above tests show that sodium sulphide on reacting with dilute $H_2SO_4$ gives $H_2S$ gas. The tests are bing explained below.

1. $Na_2S(s)+H_2SO_4(aq) \longrightarrow Na_2SO_4(aq)+H_2S(g)$.

The gas has a very distinct smell of rotten eggs. It can be recognized by its smell.

2. $(CH_3COO)_2Pb(aq)+H_2S(g) \longrightarrow 2CH_3COOH(aq)+\underset{\text{(Black)}}{PbS(s)}$

Acidic lead acetate solution turns black due to the formation of black lead sulphide. This is a characteristic test for the identification of $H_2S$ gas.

3. In a limited supply of air, free sulphur is deposited.

$$2H_2S(g)+O_2(g) \longrightarrow 2H_2O(l)+2S(s)$$

Gas is not a supporter of combution but itself burns in air with a pale blue flame. $H_2S$ gas acts as a reducing agent.

4. $2KMnO_4(aq)+3H_2SO_4(aq)+5H_2S(g) \longrightarrow K_2SO_4(aq)$

$$2\underset{\text{(Colourless)}}{MnSO_4(aq)}+8H_2OH(l)+5S(s)$$

Potassium permanganate solution decolourizes on reacting with $H_2S$ gas. This test shows that $H_2S$ gas is a strong reducing agent.

5. $Br_2(aq)+H_2S(g) \longrightarrow 2HBr(aq)+S(s)$.

Bromine solution gets decolourized and turbidity appears because sulphur is formed. This reaction also shows the strong reducing nature of $H_2S$.

6. The reaction occurs because sulphide ions form with sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, the red-violet complex $Na_4[Fe(CN)_5NOS]$ in alkaline solution.

(*v*) **Sodium sulphite, $Na_2SO_3$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A colourless gas with suffocating odour of burning sulphur is evolved. |
| 2. Pass the gas through acidified potassium dichromate solution. | The solution of potassium dichromate turns green. |
| 3. Pass the gas through acidified solution of potassium permanganate. | The acidified solution of potassium permanganate turns colourless. |
| 4. Introduce one or two petals into a test tube filled with gas. | The petals get bleached. |

**Explanation.** The observations made in the above tests show that the sodium sulphite on reacting with dilute sulphuric acid gives $SO_2$ gas. The tests employed for the identification of the gas are explained below :

1. $Na_2SO_3(s)+H_2SO_4(aq) \longrightarrow Na_2SO_4(aq)+H_2O(l)+SO_2(g)$

The gas has a very distinct suffocating odour of burning sulphur.

2. $K_2Cr_2O_7(aq)+H_2SO_4(aq)+3SO_2(g) \longrightarrow K_2SO_4(aq) + \underset{\text{(Green Colour)}}{Cr_2(SO_4)_3(aq)}+H_2O(l)$

Potassium dichromate solution decolourizes on reacting with $SO_2$ gas.

This test shows that $SO_2$ gas is a strong reducing agent.

3. $2KMnO_4(aq)+2H_2O(l)+5SO_2(g) \longrightarrow K_2SO_4(aq) + \underset{\text{(Colourless)}}{2MnSO_4(aq)}+2H_2SO_4(aq)$

Potassium permanganate solution gets decolourized giving a colourless solution of manganous sulphate. The test shows that $SO_2$ acts as a strong reducing agent.

4. $SO_2(g)+2H_2O(l) \longrightarrow H_2SO_4(aq)+\underset{\substack{\text{Nascent}\\ \text{hydrogen}}}{2H(g)}$

$$2H+\text{flower} \longrightarrow \text{Colourless.}$$

The bleaching action is due to the reduction of colours of the petals by nascent hydrogen which is formed when $SO_2$ reacts with water. Hence, it only bleaches moist materials. The bleached product slowly regains its colour on exposing to air due to oxidation.

**(vi) Sodium thiosulphate $Na_2S_2O_3$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A colourless, gas with suffocating adour of burning sulphur is evolved. Bits of sulphur appear and the solution becomes turbid. |
| 2. Perform the tests listed under. $Na_2SO_3$. | |

The explanatian of the above test is lined below :

$$Na_2S_2O_3(s)+H_2SO_4(aq) \longrightarrow H_2S_2O_3(aq)+Na_2SO_4(aq)$$

$$\underset{\text{(Unstable)}}{H_2S_2O_3(aq)} \longrightarrow H_2O(l)+S(s)+SO_2(g)$$

The reaction with salt forms thiosulpluric acid which being unstable decomposes to form $SO_2$ and S (also colloidal S). Colloidal sulphur is identified with the turbidity in the solution. Sulphur dioxide can be identified by the test employed under sodium sulphite.

**Experiment 7.2.** To identify the gases evolved when concontrated sulphuric acid reacts with (*i*) NaCl, (*ii*) NaBr, (*iii*) $NaNO_3$, and (*iv*) NaI (in hot condition).

**Apparatus.** As listed in Experiment 7.1.

**Chemicals.** NaCl, NaBr, NaI, $NaNO_3$, conc. $H_2SO_4$.

**Procedure.** Treat a small amount of salt ($\sim$2 g) with about 3 ml of concentrated sulphuric acid in a test tube. Note the reaction in the cold and then warm if necessary. Identify the gases evolved as given under :

(*i*) **Sodium chloride, NaCl**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A colourless gas with choking smell is evolved. |
| 2. Bring a glass rod carrying a drop of aquous ammonia near the mouth of test tube. | Dense white fumes are formed. |
| 3. Pass the gas through water for long and introduce a small piece of blue litmus paper into the aqueous solution of the gas contained in a test tube. | Blue litmus paper turns red. |
| 4. Pass the gas through silver nitrate solution | A white ppt. is formed. |
| 5. Treat the mixture of salt and manganese dioxide with conc. sulphuric acid and heat gently. | Effervesence takes place and a greenish yellow gas with pungent small is evolved. |
| 6. Take a small amount of salt in a test tube, and add 0.5 ml of conc. $KMnO_4$ solution and 2 ml of conc. $H_2SO_4$. Heat the mixture gently. | Potassium permanganate solution gets decolourized and a greenish yellow gas with pungent smell is evolved. |

**Explanation**. The observations made in the above tests show that the sodium chloride on reacting with conc. sulphuric acid gives hydrogen chloride gas. The tests employed for the identification of the gas are explained below :

1. $2NaCl(s)+H_2SO_4(aq) \longrightarrow Na_2SO_4(aq)+2HCl(g)$

The gas has a distinct pungent small.

2. $NH_4OH(aq)+HCl(g) \longrightarrow NH_4Cl(g)+H_2O(l)$

Aqueous ammonia on reacting with the gas forms dense white fumes, (smoke) which characterizes the formation of ammonium chloride.

3. Dry gas does not turn blue litmus red.

When dissolved in water, hydrogen chloride solution turns blue litmus red and, hence, is acidic in nature. In aqueous solution of HCl gas, $H^+$ and $Cl^-$ ions exist. $H^+$ ions exist as $H_3O^+(aq)$ known as hydronium ion.

$$HCl(aq)+H_2O(l) \longrightarrow H_3O^+(aq)+Cl^-(aq)$$

Due to the presence of $H_3O^+(aq)$ ions, hydrochloric acid exhibits all acidic properties. It conducts electricity.

4. $AgNO_3(aq)+HCl(g) \longrightarrow \underset{\text{(White ppt.)}}{AgCl(s)} + HNO_3(aq)$

Silver nitrate on reacting with the gas forms greyish white ppt., a distinct property of AgCl.

The white precipitate of AgCl dissolves in aqueous ammonia due to the complex formation.

$$AgCl(s)+2NH_3(aq) \longrightarrow \underset{\substack{\text{Diammine silver}\\ \text{chloride}}}{[Ag(NH_3)_2]Cl}$$

Precipitation of AgCl is usually done in the presence of dilute $HNO_3$. The precipitate does not dissolve in dilute $HNO_3$. This can be used as a test for hydrogen chloride or hydrochloric acid.

5. $MnO_2(s)+4HCl(aq) \longrightarrow MnCl_2(aq)+2H_2O(l)+Cl_2(g)$

Aqueous hydrogen chloride solution reacts with manganese oxide, an oxidizing agent forming a greenish yellow gas, *i.e.*, chlorine gas. Here, HCl reduces manganese dioxide and is itself oxidized to chlorine gas, which is recognized by its distinct odour and colour. The gas can be identified by a moist iodized starch paper. In the presence of the gas, dark blue colour appears because of the formation of iodine.

$$2KI+Cl_2 \longrightarrow 2KCl+I_2$$

6. $2KMnO_4(aq)+16HCl(aq) \longrightarrow 2KCl(aq)+10MnCl_2(aq)$
$+8H_2O(l)+5Cl_2(g)$

$KMnO_4$ solution gets decolourized and a distinct greenish yellow coloured gas is evolved, which can be identified by the test listed under 5. It confirms that chlorine gas is an oxidizing agent.

(*ii*) **Sodium bromide, NaBr**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | Intense brown vapours are evolved. Vapours appear to be of bromine. |
| 2. Expose the starch paper impregnated with potassium iodide solution. | Starch paper becomes blue in colour. |
| 3. Pass the gas through $AgNO_3$ solution for long. | Light yellowish curdid ppt. |
| 4. Take a small amount of salt in a test tube and add 1 ml of conc. $H_2SO_4$. Warm gently. New add 1 ml of carbon tetrachloride follow by a few drops of chlorine water and shake well. | The organic layer becomes reddish yellow. |
| 5. Treat the mixture of salt and manganese dioxide with conc. $H_2SO_4$ and heat gently. | Effervesence takes place and a brown gas with a pungent smell is evolved. |
| To the same tube add one ml of $CCl_4$ and shkae well. | The organic layer becomes reddish yellow. |
| 6. Pass the gas through acidified dilute solution of potassium dichromate. | It acquires a slight greenish tinge. |

**Explanation.** The observations made in the above tests show that hydrogen bromide, bromine and sulphur dioxide are formed when salts of hydrobromic acid (bromides) are heated with conc. $H_2SO_4$. The tests employed for the identification of the gases are explained below :

$$1.\quad NaBr(s)+H_2SO_4(aq) \longrightarrow NaHSO_4(s)+HBr(g)$$

$$2HBr(g)+H_2SO_4(aq) \longrightarrow 2H_2O(l)+SO_2(g)+Br_2(g)$$

The mixture of these gases looks brown due to the brown colour of bromine gas. Both HBr and $SO_2$ are colourless gases. The mixture of these gases gives a very pungent smell. The two gases, *i e.* $Br_2$ and $SO_2$ are produced during the course of reaction because HBr reduces $H_2SO_4$ to $SO_2$ and is itself oxidized to $Br_2$.

2. When starch paper impregnated with potassium iodide is exposed to the gas, it develops blue colour. This is because $Br_2$ gas acts as an oxidizing agent and liberates $I_2$ which reacts with starch.

3. $AgNO_3(aq) + HBr(g) \longrightarrow \underset{\text{(Yellow ppt.)}}{AgBr(s)} + HNO_3(aq)$

HBr forms yellow precipitate with silver nitrate solution. The yellow ppt. of AgBr is partially soluble in aqueous ammonia due to complex formation as given under sodium chloride.

4. Organic solvent, *i.e.*, carbon tetrachloride extracts bromine which is formed during the course of reaction. The organic solvent layer becomes yellow, red or brown in the presence of bromine, depending on the concentration of bromine and on the solvent.

5. $2NaBr(s) + MnO_2(s) + 3H_2SO_4(aq)$
$\longrightarrow 2NaHSO_4(s) + MnSO_4(aq) + 2H_2O(l) + Br_2(g)$

Aqueous hydrogen bromide solution reacts with manganese dioxide, an oxidizing agent forming a brown coloured gas, *i.e.*, bromine gas. This gas is moderately soluble in water. Here, HBr reduces manganese dioxide and is itself oxidized to $Br_2$. Organic solvent extracts $Br_2$ which is produced in the reaction.

6. Potassium dichromate solution acquires a tinge of green colour due to the its reduction to chromic sulphate (green colour) by $SO_2$ a reducing agent. $SO_2$ is formed when NaBr is reacted with conc. $H_2SO_4$. (Ref. Test 1).

(*ii*) **Sodium nitrate, $NaNO_3$**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | A brown coloured gas is evolved. |
| 2. Add copper turnings to the test tube used in the test 1 and heat. | Deep brown fumes in plenty are evolved. |
| 3. Pass the gas through potassium iodide solution. | Violet fumes are evolved. Solution also acquires colour. |
| 4. Pass the gas through acidified ferrous sulphate. | The solution turns brown. |

**Explanation.** The observations made in the above tests confirm that nitrogen dioxide (brown coloured) gas is formed when salts of nitric acid (nitrates) decompose. The tests employed to identify the gas are explained below :

1. $NaNO_3(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(s) + HNO_3(aq)$

$$4HNO_3(aq) \xrightarrow{H_2SO_4} 4NO_2(s) + 2H_2O(l) + O_2(g)$$

The gas is recognized by its reddish brown colour and pungent smell.

2. The gas formed during the course of reaction dissolves in the solution ($NO_2$ is soluble in water) forming nitric acid which oxidizes copper to form copper nitrate and more of nitrogen dioxide gas. As a result, dense brown fumes are formed.

$$2NO_2(aq)+H_2O(l) \longrightarrow HNO_3(aq)+HNO_2(aq)$$

$$Cu(s)+4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq)+2H_2O(l)+2NO_2(g)$$

$$Cu(s)+8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq)+4H_2O(l)+2NO(g)$$

3. $2KI(aq)+NO_2(s) \longrightarrow 2KNO_2+I_2$

The evolution of iodine is confirmed by exposing a piece of filter paper impregnated with starch solution. Paper acquires deep blue colour due to the absorption of iodine. This test shows that nitrogen dioxide gas acts as an oxidizing agent.

4. $2FeSO_4(aq)+H_2SO_4(aq)+NO_2(g)$

$$\longrightarrow Fe_2(SO_4)_3(aq)+NO(g)+H_2O(l)$$

$$FeSO_4(aq)+5H_2O+NO(g) \longrightarrow \underset{\text{(Black)}}{[Fe(H_2O)_5(NO)]SO_4}$$

The reaction is based on the reduction of nitrogen dioxide to nitric oxide by ferrous sulphate ; nitric oxide with excess ferrous sulphate forms an unstable complex which forms the solution black.

(*iv*) **Sodium iodide, NaI**

| *Experiment or Test* | *Observation* |
|---|---|
| 1. Observe the reaction and the gas evolved. | Violet vapours are evolved. |
| 2. Expose a piece of filter paper impregnated with starch solution. | Starch paper becomes blue in colour. |
| 3. Pass the gas through $AgNO_3$ solution for long. | Yellowish curdid ppt. |
| 4. Take a small amount of salt in a test tube and add 1 ml of conc. $H_2SO_4$. Heat the contents. Now add 1 ml of carbon tetrachloride followed by a few drops of chlorine water and shake well. | The organic layer acquires violet colour. |
| 5. Treat the mixture of salt and manganese dioxide with conc. $H_2SO_4$ and heat gently. | Effervescence takes place and deep violet vapours are evolved. |
| 6. Pass the gas through acidified dilute solution of potassium dichromate. | It acquires a slight greenish tinge. |

**Explanation.** The observations made in the above tests confirm that hydrogen iodide, iodine and sulphur dioxide are formed when salts of hydriodic acid (iodides) are heated with conc. $H_2SO_4$. The explanation of the tests is given below :

1. $NaI(aq)+H_2SO_4(aq) \longrightarrow NaHSO_4(s)+HI(g)$

$$2HI(g)+H_2SO_4(aq) \longrightarrow 2H_2O(l)+I_2(g)+SO_2(g)$$

The mixture of these gases looks violet in colour due to the intense violet colour of the iodine vapours. Both HI and $SO_2$ are colourless gases. The mixture of these gases gives a very irritating smell. $I_2$ and HBr are produced during the course of reaction because HI on heating reduces $H_2SO_4$ to $SO_2$ and is itself is oxidized to iodine.

2. The free iodine can be detected by the formation of violet vapours and also by the blue colour of starch paper.

3. $AgNO_3(aq)+HI(g) \longrightarrow \underset{\text{(Yellow ppt.)}}{AgI(s)} + HNO_3(g)$

HI reacts with silver nitrate solution, forming yellow ppt. of AgI, which is insoluble in aqueous ammonia.

4. Organic solvent, *i.e.*, carbon tetrachloride, etc., extracts iodine formed in the reaction. The organic layer acquires reddish violet colour.

5. $2NaI(s)+MnO_2(s)+3H_2SO_4(aq)$
$\longrightarrow 2KHSO_4(s)+MnSO_4(aq)+2H_2O(l)+I_2(g)$

Aqueous hydrogen iodide solution reacts with manganese dioxide producing violet vapours of iodine. Here HI reduces $MnO_2$ and is itself oxidized to iodine. Organic layer extracts iodine which is produced in the reaction.

6. Potassium dichromate solution acquires a tinge of green colour due to its reduction to chromic sulphate (green colour) by sulphur dioxide, a reducing agent. $SO_2$ is formed in the reaction of sodium iodide with hot conc. $H_2SO_4$.

## ORAL QUESTIONS AND ANSWERS

**Q. 7.1.** What happens when carbon dioxide is bubbled through lime water for a long time ?

**Ans.** When excess of $CO_2$ gas is passed for a long time through lime water, the white ppt. of calcium carbonate is first formed which disappears again, as $CaCO_3$ is converted into the soluble calcium bicarbonate.

$$Ca(OH)_2(aq)+CO_2(g) \longrightarrow \underset{\text{(White ppt.)}}{CaCO_3(s)}+H_2O(l)$$

$$CaCO_3(s)+H_2O(l)+CO_2(g) \longrightarrow \underset{\text{(soluble)}}{Ca(HCO_3)_2(aq)}$$

**Q. 7.2.** Can dil. $H_2SO_4$ be replaced by dil. $HNO_3$ in preparation of $H_2S$ gas ?

**Ans.** We cannot use dil. $HNO_3$ in the preparation of $H_2S$ gas as nitric acid oxidizes the $H_2S$ gas produced.

$$FeS(s)+2HNO_3(l) \longrightarrow Fe(NO_3)_2(aq)+H_2S(g)$$
$$2HNO_3(aq) \longrightarrow H_2O(l)+2NO_2(g)+[O]$$
$$H_2S(g)+[O] \longrightarrow H_2O(l)+S(s)$$

**Q. 7.3** Why can $H_2S$ gas be not dried by passing through conc. $H_2SO_4$ ?

**Ans.** Conc. $H_2SO_4$ cannot be used as a drying agent for $H_2S$ gas as it is reduced by the gas.

$$H_2SO_4(aq) \longrightarrow SO_2(g)+H_2O(l)+[O]$$
$$H_2S(g)+[O] \longrightarrow S(s)+H_2O(l)$$
$$\overline{H_2SO_4(aq)+H_2S(g) \longrightarrow SO_2(g)+2H_2O(l)+S(s)}$$

**Q. 7.4.** Why can dry chlorine gas be not used as a bleaching agent ?

**Ans.** Chlorine bleaches only in the presence of moisture as it combines with it to produce nascent oxygen which has got bleaching action.

$$Cl_2(g)+H_2O(l) \longrightarrow 2HCl(g)+[O]$$

**Q. 7.5.** Can chlorine gas be used as a bleaching agent for silk, wool etc. ?

**Ans.** It should not be used as a bleaching agent for these types of delicate fibres as they are damaged by chlorine.

**Q. 7.6.** Show the acidic nature of sulphur dioxide in solution ?

**Ans.** Sulphur dioxide dissolves in water to give sulphurous acid which ionizes as given below :

$$SO_2(g)+H_2O(l) \longrightarrow H_2SO_3(l) \rightleftharpoons 2H^+ + SO_3^{2-}$$

Its solution turns moist blue litmus paper red.

**Q. 7.7.** You are provided with two jars one containing $CO_2$ gas and another containing CO gas, how will you distinguish ?

**Ans.** CO gas burns with blue flame and will not change the colour of lime water while $CO_2$ gas will make the lime water milky.

**Q. 7.8.** How will you distinguish between the jars of $H_2S$ gas and $SO_2$ gas ?

**Ans.** $H_2S$ gas jar will turn lead acetate paper black and produce violet colour with ammoniacal sodium nitroprusside.

$SO_2$ gas jar will turn potassium dichromate paper green.

**Q. 7.8.** Explain the bleaching action of sulphur dioxide.

**Ans.** The bleaching action is due to the reduction of the colours of substances by nascent hydrogen which is formed when $SO_2$ reacts with water. Hence, it only bleaches moist materials.

$$SO_2(g)+2H_2O(l) \longrightarrow H_2SO_4(aq)+\underset{\text{Nascent hydrogen}}{2[H]}$$

Its bleaching action is temporary and mild. Hence, it is used for delicate things such as flowers, wool, etc. It can also bleach sugar, straw, paper, etc. The bleaching action also confirms the reducing nature of sulphur dioxide.

The bleached product slowly regains its colour on exposing to air due to oxidation.

$$\text{Bleached product}+\text{Atmospheric oxygen}\xrightarrow{\text{Oxidation}}\text{Original product}$$

**Q. 7.9.** Explain the acidic nature of $H_2S$ gas.

**Ans.** It is fairly soluble in water and its solution is weakly acidic in nature. The acidity is caused by the slight ionization of the dissolved gas to give hydrogen ions (or hydronium ions). It turns blue litmus paper red.

$$H_2S+H_2O \longrightarrow H_3O^+ + \underset{\text{Hydrosulphide ion}}{HS^-}$$

$$H_2O+HS^- \longrightarrow \underset{\text{Hydronium ion}}{H_3O^+} + \underset{\text{Sulphide ion}}{S^{2-}}$$

**Q. 7.10.** How does $H_2S$ react with various metal salt solutions ?

**Ans.** $H_2S$ reacts with many salt solutions forming insoluble coloured sulphides. Some sulphides are precipitated in acidic medium and some others are precipitated in alkaline medium. When $H_2S$ is bubbled through a solution of lead acetate or lead nitrate it turns black due to the precipitation of lead sulphide (PbS).

$$Pb(NO_3)_2(aq)+H_2S(g) \longrightarrow \underset{\text{(Black)}}{PbS(s)}+2HNO_3(aq)$$

$$Pb(CH_3COO)_2(aq)+H_2S(g) \longrightarrow \underset{\text{(Black)}}{PbS(s)}+\underset{\text{Acetic acid}}{2HOOCCH_3(aq)}$$

In a similar fashion, $H_2S$ reacts with other metal salt solutions. In acidic medium

$$CuSO_4(aq)+H_2S(g) \longrightarrow \underset{\text{(Black)}}{CuS(s)}+H_2SO_4(aq)$$

$$CdSO_4(aq)+H_2S(g) \longrightarrow \underset{\text{(Yellow)}}{CdS(s)}+H_2SO_4(aq)$$

$$HgCl_2(aq)+H_2S(g) \longrightarrow \underset{\text{(Black)}}{HgS(s)}+2HCl(aq)$$

In alkaline medium

$$ZnSO_4(aq)+H_2S(g) \longrightarrow \underset{\text{(White)}}{ZnS(s)}+H_2SO_4(aq)$$

$$NiSO_4(aq)+H_2S(g) \longrightarrow \underset{\text{(Black)}}{NiS(s)}+H_2SO_4(aq)$$

$$MnSO_4(aq)+H_2S(g) \longrightarrow \underset{\text{(Buff)}}{MnS(s)}+H_2SO_4(aq)$$

Such reactions of hydrogen sulphide are used in qualitative inorganic analysis for identifying the various metallic ions.

**Q. 7.11.** Explain the reducing nature of sulphur dioxide.

**Ans.** Sulphur dioxide acts as a reducing agent in the presence of moisture because it is easily oxidized to sulphuric acid liberating nascent hydrogen.

$$SO_2(g)+2H_2O(l) \longrightarrow H_2SO_4(aq)+2[H]$$

(*i*) It reduces halogens to halogen acids. When sulphur dioxide is bubbled through a pale green solution of chlorine water, the gas is absorbed. The chlorine water turns colourless forming a mixture of hydrochloric acid and sulphuric acid.

$$SO_2(g)+2H_2O(l) \longrightarrow H_2SO_4(aq)+2[H]$$

$$X_2(aq)+2[H] \longrightarrow 2HX(aq)$$

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$$SO_2(g)+X_2(aq)+2H_2O(l) \longrightarrow H_2SO_4(aq)+2HX(aq)$$

where $X = Cl$, Br or I.

An aqueous solution of $SO_2$ decolourizes the coloured solutions of bromine and iodine forming colourless corresponding halogen acids (hydracids).

(*ii*) It also reduces ferric (III) salts and acidified solutions of permanganates (VII) and dichromates (VI) to ferrous (II), manganese (II) and chromic (III) salts respectively.

$$\underset{\text{(Yellow colour)}}{2FeCl_3(aq)}+2H_2O(l)+SO_2(g)$$
$$\longrightarrow \underset{\text{(Pale green colour)}}{2FeCl_2(aq)}+2HCl(aq)+H_2SO_4(aq$$

$$\underset{\text{(Purple colour)}}{2KMnO_4(aq)}+2H_2O(l)+5SO_2(g)$$
$$\longrightarrow K_2SO_4(aq)+\underset{\text{(Colourless)}}{2MnSO_4(aq)}+2H_2SO_4(aq$$

$$\underset{\text{(Orange colour)}}{K_2Cr_2O_7(aq)}+H_2SO_4(aq)+3SO_2(g) \longrightarrow K_2SO_4(aq)+\underset{\text{(Green colour)}}{Cr_2(SO_4)_3(aq)}+H_2O$$

**Q. 7.12.** Show that chlorine is more reactive than both bromine and iodine.

**Ans.** Chlorine displaces both bromine and iodine from solutions of their salts. Bromine is red coloured. Hence, the colourless solution of KBr turns red. Iodine makes the KI solution reddish-brown solution.

$$2KBr(aq)+Cl_2(g) \longrightarrow 2KCl(aq)+Br_2(aq)$$
$$2KI(aq)+Cl_2(g) \longrightarrow 2KCl+I_2(g)$$

Iodine vapours turn a starch paper blue.

These reactions show that chlorine is more reactive than bromine and iodine.

**Q. 7.13.** How will you distinguish the halogens from each other ?

**Ans.**

**Detection of halogens**

| *Property* | *Chlorine* | *Bromine* | *Iodine* |
|---|---|---|---|
| State and colour | Greenish-yellow gas | Reddish-brown liquid | Steel grey solid |
| Smell | Pungent | Pungent | Pungent |
| Action on starch-iodide paper | Turns starch iodide paper blue | Turns starch iodide paper blue | Turns starch iodide paper violet or deep blue |
| Action on carbon disulphide | — | Dissolves giving orange-coloured solution. | Dissolves giving violet solution |

**Q. 7.14.** What happens when sulphur dioxide reacts with (*i*) Aqueous solution of iodine, (*ii*) Aqueous solution of $H_2S$, (*iii*) Alkali solution, (*iv*) Aqueous solution of $FeCl_3$, and (*v*) Colouring material present in flowers ? Give chemical equations.

**Ans.** (*i*) $I_2+2H_2O+SO_2 \longrightarrow 2HI+H_2SO_4$

(*ii*) $2H_2S+SO_2 \longrightarrow 2H_2O+3S$

(*iii*) $NaOH+SO_2 \longrightarrow NaHSO_3$

$NaHSO_3+NaOH \longrightarrow Na_2SO_3+H_2O$

(*iv*) $2FeCl_3+SO_2+2H_2O \longrightarrow 2FeCl_2+2HCl+H_2SO_4$

(*v*) Colouring matter $\xrightarrow{SO_2}$ Gets bleached

**Q. 7.15.** What happens when $Cl_2$ reacts with

(*i*) Alkali metal, (*ii*) Sulphur dioxide solution in water, (*iii*) A non-metal, (*iv*) Sodium hydroxide and (*v*) Slaked lime ?

Give equations.

**Ans.** (*i*) Molten sodium burns in chlorine with a yellow flame.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

(*ii*)

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + Cl_2 + H_2O \longrightarrow H_2SO_4 + 2HCl$$

(*iii*) White phosphorus burns spontaneously in the atmosphere of $Cl_2$ producing white fumes of chlorides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

(*iv*)

$$\underset{\text{(Cold, dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

$$\underset{\text{(Hot, conc.)}}{6NaOH} + 3Cl_2 \longrightarrow NaClO_3 + 5NaCl + 3H_2O$$

(*v*)

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

**Q. 7.15.** Distinguish between hydrogen chloride and hydrochloric acid.

**Ans.** Hydrogen chloride gas in water is called hydrochloric acid. Hydrochloric acid is present as $H^+$ and $Cl^-$ ions. Here $H^+$ exists as $H_3O^+$.

$$H_2O(l) + HCl(aq) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Due to the presence of $H_3O^+$ ions, hydrochloric acid exhibits acidic properties.

Hydrogen chloride has a single polar covalent bond. There are no $H_3O^+$, $H^+$ or $Cl^-$ ions. Thus, it does not exhibit acidic properties.

**Q. 7.16.** Distinguish between the bleaching action of sulphur dioxide and chlorine.

**Ans.** (*i*) Both sulphur dioxide and chlorine act as bleaching agents in presence of water. Dry gases do not bleach.

(*ii*) Bleaching by sulphur dioxide is by reduction. Oxygen is removed from the colouring matter present in the article.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$H_2SO_3$ + O (from colouring matter) → $H_2SO_4$ + colourless compound. Bleaching by chlorine is by oxidation when oxygen combines with the colouring matter present in the article.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$HOCl \longrightarrow HCl + O$$

$$O + (\text{colouring matter}) \longrightarrow \text{Colourless substance}$$

(*iii*) The bleaching by sulphur dioxide is temporary but the bleaching by chlorine is permanent. □ □

## UNIT 8

# Qualitative Analysis of Inorganic Salts—Indentification of Cations and Anions

### 8.1. Introduction

A substance is analyzed to establish its qualitative or quantitative (Unit 9) chemical composition. An anyalsis that yields information only as to the identity of the ingredients is known as qualitative analysis. Qualitative analysis of inorganic substances is primarily concerned with the detection and identification of the ions present in a substance (a single substance/salt or a mixture of substances/salts). The salts, on dissolution in water, spilt into positively charged ions called cations and negatively charged ions called anions. The cation is also known as basic radical and the anion as acid radical.

In qualitative analysis, in order to identify the ions of a substance being analyzed, other substances (solids, solutions, etc.) called reagents are added to it that cause chemical transformations accompanied with the formation of new compounds possessing specific properties : a definite physical state (precipitate, liquid gas) ; certain solubility in water, acids, alkalis and other chemical solvents, a characteristic colour, odour and so forth.

The following principles has a great bearing upon the operations usually followed in qualitative analysis, law of mass action, common ion effect, solubility product, complex ion formation, pH, etc.

A reaction used in qualitative analysis must :

1. occur rapidly, practically instantanously,

2. be accompanied with the formation of a characteristic precipitate, gas or with the appearance of a colour,

3. be practically irrevesible, *i.e.*, occur mainly in one direction, and

4. be specific, if possible, and highly sensitive.

In our scheme of qualitative analysis, we shall analyze the salts for the following cations and anions :

**Cations**. Lead (*ii*) $Pb^{2+}$, mercury (*ii*) $Hg^{2+}$, copper (*iii*) $Cu^{2+}$, cadmium (*ii*) $Cd^{2+}$, arsenic (*iii*) $As^{3+}$, antimony (*iii*) $Sb^{3+}$, iron (*ii*)

$Fe^{2+}$, iron (*iii*) $Fe^{3+}$, aluminium (*iii*) $Al^{3+}$, nickel (*iii*) $Ni^{2+}$, cobalt (*ii*) $Co^{2+}$, manganese (*ii*) $Mn^{2+}$, zinc (*ii*) $Zn^{2+}$, calcium (*ii*) $Ca^{2+}$, barium (*ii*) $Ba^{2+}$, strontium (*ii*) $Sr^{2+}$, magnesium (*ii*) $Mg^{2+}$, potassium (*i*) $K^+$, ammonium (*i*) $NH_4^+$ and sodium (*i*) $Na^+$.

**Anions**. Carbonate, $CO_3^{2-}$, sulphite, $SO_2^{2-}$, sulphide $S^{2-}$, chloride $Cl^-$, bromide $Br^-$, iodide, $I^-$, nitrite, $NO_2^-$ nitrate, $NO_3^-$, sulphate $SO_4^{2-}$, phosphate $SO_4^{3-}$ and acetate $CH_3COO^-$.

## 8.2. Systematic Analysis

The salt analysis may be systematically carried out in the following steps :

(*i*) Preliminary examination,

(*ii*) Detection of anions, and

(*iii*) Detection of cations.

## 8.3. Preliminary Examination

In qualitative analysis, various characteristic features of the chemical substances being analyzed are used for establishing its chemical composition. For example, ammonia can easily be identified by its chasacteristic smell and ammonium salts, by the liberation of ammonia gas when then salts are heated with caustic soda.

In some cases, substances are tested by dry analysis, *i.e.*, without transferring thein into solution. Such an analysis usually consists the examination of physical properties of the salt. It involves the heating of a substance to give a gas with a distinct smell and colour. It also consists in testing the ability of a salt to give a characteristic colour to a colourless flame or a certain colour to a melt (bead or glass) obtained when heating the substance with borax in the eye of platinum wire.

### 8.3.1. Physical properties

The physical properties of a salt, *viz.*, colour, appearance and odour etc. help in arriving at an inference regarding the salt as given in Table 8.1.

### 8.3.2. Action of heat

A substance on heating may sublime, decompose with evolution of gas, or undergo certain other changes. Careful observation of the changes and recognition of the gases evolved help us in arriving at some result (Table 8.2).

Further the colour of a salt indicates its constituents, *e.g.*, copper carbonate is green, copper sulphide is black, cadmium sulphide is yellow, ferric hydroxide is brown and manganese sulphate is pink.

**Table 8.1. Physical properties of salts**

| *Physical property* | *Inference* |
|---|---|
| White colour (colourless) | $Pb^{2+}$, $Al^{3+}$, $Zn^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Mg^{2+}$ or $NH_4^+$ salt may be present |
| Bluish or bluish green colour | $Cu^{2+}$ or $Ni^{2+}$ salt |
| Light green colour | $Fe^{2+}$ or $Ni^{2+}$ salt |
| Yellowish brown colour | $Fe^{3+}$ salt |
| Light pink/buff colour | $Mn^{2+}$ salt |
| Pnik or dark pink | $CO^{2+}$ salt |
| Smell of ammonia gas | $NH_4^+$ salt |
| Smell of hydrogen sulphide gas | $S^{2-}$ salt |
| Smell of sulphur dioxide gas | $SO_3^{2-}$ salt |
| Deliquescent nature | $Cl^-$ or $NO_3^-$ salt may be present. |

**Table 8.2. Action of heat on salts**

| *Observation* | *Inference* | *Chemistry involved* |
|---|---|---|
| Salt appears to be melting | Presence of some hydrated salt | Hydrated salt dissolves in its water of crystallization and appears to have melted. |
| White sublimate | $NH_4^+$ salt may be present | Some ammonium salts decompose on heating leaving behind a sublimate :<br>$(NH_4)_2SO_4(s) \longrightarrow NH_3(g) + NH_4HSO_4(s)$ |
| Ammonia evolves, detected by smell | $NH_4^+$ salt | Ammonium salts decompose on heating to give ammonia :<br>$(NH_4)_2CO_3(s) \longrightarrow NH_3(g) + CO_2(s) + H_2O(g)$ |
| Carbon dioxide gas evolves detected by allowing the gas to pass through lime water | Lime water turns milky<br>$CO_3^{2-}$ present | Carbonates decompose on heating to give carbon dioxide :<br>$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$<br>$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ |
| Sulphur dioxide gas evolves, detected by a filter paper soaked in $K_2Cr_2O_7$ solution | Paper turns green<br>$SO_3^{2-}$ or $SO_4^{2-}$ may be present | Some sulphites and sulphates decompose to give sulphur dioxide :<br>$2FeSO_4(s) \longrightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$<br>$2CuSO_4(s) \longrightarrow 2CuO(s) + 2SO_2(g) + O_2(g)$ |
| Nitrogen dioxide gas evolves, detected by its colour and irritating smell | $NO_3^-$ present | Nitrates decompose to give nitrogen dioxide :<br>$2Cu(NO_3)_2(s) \longrightarrow 2CuO(s) + O_2(g) + 4NO_2(g)$ |
| Colour of the salt changes from | | |
| (*i*) blue to white | $Cu^{2+}$ salt | Some salts change the colour either by losing water of crystallization or due to the change in state :<br>$\underset{\text{(blue)}}{CuSO_4.5H_2O(s)} \longrightarrow \underset{\text{(white)}}{CuSO_4(s)} + 5H_2O(s)$ |
| (*ii*) green to yellow | $Ni^{2+}$ salt | |
| (*iii*) yellow (when hot) to white (when cold) | $Zn^{2+}$ salt | |

### 8.3.3 Flame test

Salts of some elements can be identified by the colour which they impart to the colourless flame of burner ; sodium salts turn it yellow ; potassium salts, violet ; calcium salts, brick red, barium salts, green ; copper salts, blue-green ; and so forth. Thus, this property can be helpful in identifying the various metal ions. For a particular element the flame colouration remains the same irrespective of whether the element is in the free state or combined with other elements. For example, metallic copper, copper sulphate, copper nitrate, copper chloride and copper carbonate all impart blue-green colour to the flame The colour is characteristic of copper in all its forms. The flame test is usually carried out with the chloride of the metal as it is more volatile than other salts. The given salt is treated with concentrated hydrochloric acid (to convert it into the chloride form) and placed in the eye of platinum or nichrome wire. The wire is then heated in an oxidizing (non-luminous) flame when it imparts a characteristic colour to the flame (Table 8.3). Platinum or nichrome wire is suitable for the flame test because it neither melts nor imparts colour to the flame. Ordinary salts may be associated with an impurity of a sodium salt and give a yellow flame of short duration. To overcome this difficulty, the flame may also be viewed through blue glass (cobalt glass) which absorbs the yellow sodium light.

**Table 8.3. Flame test**

| *Flame colour by naked eye* | *Flame colour through blue glass* | *Inference* |
|---|---|---|
| Deep blue green | Bluish green | $Cu^{2+}$ |
| Brick red | Light yellow | $Ca^{2+}$ |
| Apple green | Bluish green | $Ba^{2+}$ |
| Crimson (deep red) | Purple | $Sr^{2+}$ |
| Violet | Pink | $K^{+}$ |

**Procedure for the flame test**. Make a circular loop (eye) at the end of a platinum (or nichrome) wire sealed in a glass tube. Dip it into concentiated hydrochloric acid and heat it in a non-luminous flame. Repeat this process until the platinum wire imparts no colour to the flame.

Prepare a paste of the salt with conc. hydrochloric acid in a watch glass Take a small amount of the paste in the eye of the wire and heat in the oxidizing flame (Fig. 8·1). The salt melts in the burner flame, forming a bead. The bead is dipped for an instant into paste. Chloride compounds being volatile produce a coloured flame. First observe the colour imparted to the flame with the naked eye and then through the blue glass.

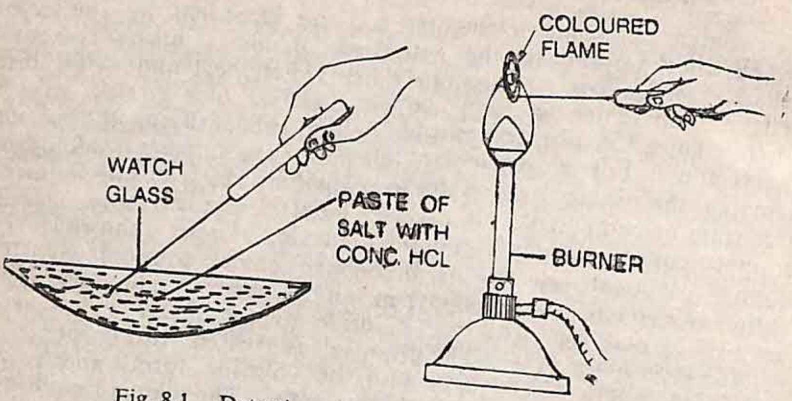


Fig. 8.1. Detection of some elements by flame test—carrying out a test.

**Notes about flame test**

1. The order of appearance of colour in the flame is (*i*) $Na^+$, (*ii*) $K^+$, (*iii*) $Cu^{2+}$, (*iv*) $Ca^{2+}$, (*v*) $Sr^{2+}$ and (*vi*) $Ba^{2+}$.

2. Persistent golden yellow colour of sodium usually conceals all other colours of flames. When all the sodium is removed, the other flames make their appearance.

3. Everytime this test should be performed with a thoroughly cleaned wire, so that any salt adhering to it does not impart its colour to the flame.

4. Never dip the platinum wire into the bottle of conc. HCl for cleaning it. Always use a few ml of the conc. acid in a test tube for this purpose. The acid after use should be thrown into the sink.

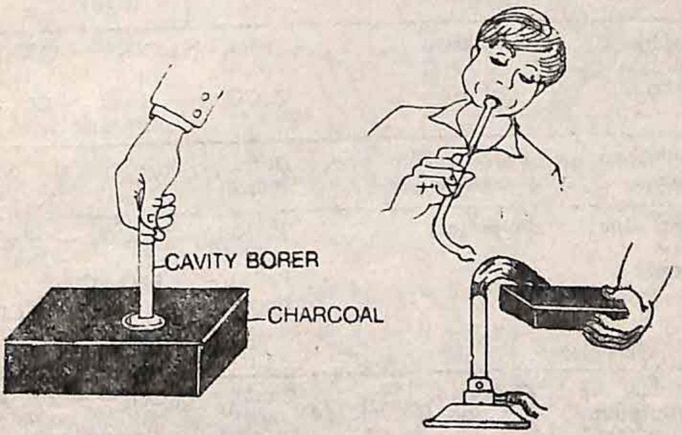
5. Do not use the acid, which is employed for cleaning platinum wire, for making paste of mixture.

### 8.3.4. Charcoal cavity test

This test is carried out for the detection of the cation present in a salt. On heating the mixture of the salt and sodium carbonate (or fusion mixture) in a charcoal cavity, the metal carbonate is formed by double decomposition. The carbonate on further heating decomposes to the oxide, which is left as a coloured residue in the cavity. The colour of the residue is characteristic of the metal present. The metallic oxide, at times, is reduced to the metal by the reducing action of the charcoal resulting in the formation of metallic bead. The metal formed may also form an oxide with oxygen present in air. The oxide deposits in the form of layer or crust around the cavity called incrustation. The colour of the residue, bead or incrustation helps in identifying the metal.

**Procedure for charcoal cavity test.** Make a small cavity in a charcoal-block with a knife or cavity borer (Fig. 8.2*a*). Fill the cavity with the mixture of the salt (1 part) and sodium carbonate or fusion mixture (2 parts).

Moisten the mixture with a drop of water. Hold the charcoal block in the left hand and deflect the reducing flame* upon it with the help of a blow-pipe for about two minutes (Fig. 8.2*b*). Observe the colour of the incrustation (a crust around the cavity) and the residue (hot and cold). At time metallic bead formation takes place. Draw the inference (Table 8.4).



(*a*) Making cavity (*b*) Performing charcoal-cavity test

Fig. 8.2.

**Notes about charcoal cavity**

1. Always make a fresh cavity for a fresh salt.

2. While making a cavity do not apply pressure otherwise it is likely to crack.

3. Do not make a very deep cavity and there should be some space around it for incrustation to form.

4. While performing charcoal cavity test always moisten the mixture with a drop of water otherwise the mixture is likely to be blown away.

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*To obtain a *reducing flame* make the bunsen-burner flame luminous by closing the air holes of the burner. Keep the nozzle of the blow pipe just outside the flame and blow gently on to the cavity.

**Table 8.4. Charcoal cavity test**

| *Observation* | *Inference* | *Chemistry involved* |
|---|---|---|
| White residue, no incrustation | Al, Ca, Ba, Sr or Mg present | Corresponding metal oxide forms *e.g.*<br>$2Al + 3O_2 \longrightarrow Al_2O_3$ |
| Red residue, no incrustation | Cu present | $CuSO_4 + NaCO_2 \longrightarrow CuCO_3 + Na_2SO_4$<br>$CuCO_3 \longrightarrow CuO + CO_2$<br>$CuO + C \longrightarrow \underset{\text{(Red)}}{Cu} + CO$ |
| Brown residue, brown incrustation | Cd present | $CdSO_4 + Na_2CO_3 \longrightarrow CdCO_3 + Na_2SO_4$<br>$CdCO_3 \longrightarrow \underset{\text{(Brown)}}{CdO} + CO_2$ |
| Black residue, no incrustation | Fe, Ni or Mn present | Corresponding metal oxide forms |
| Shinning metallic bead, yellow incrustation | Pb present | $Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$<br>$PbCO_3 \longrightarrow PbO + CO_2$<br>$PbO + C \longrightarrow \underset{\text{(Metallic bead)}}{Pb} + CO$ |
| Yellow residue, and yellow incrustation (when hot), white residue and white incrustation (when cold) | Zn present | $ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$<br>$ZnCO_3 \longrightarrow \underset{\text{(Residue)}}{ZnO} + CO_2$<br>$ZnO + C \longrightarrow Zn + CO$<br>$2Zn + O_2 \longrightarrow \underset{\text{(Incrustation)}}{2ZnO}$ |

### 8.3.5. Cobalt nitrate test

This is an extension of the charcoal cavity test. This test is performed only when a white residue is formed in the cavity. Add a drop of cobalt nitrate solution over the white residue. Heat it again in the non-luminous (oxidizing) flame with the help of a blow pipe. Note the colour of the residue formed and draw the inference (Table 8.5).

### 8.3.6. Borax-bead test

This test is used for detection of cations in coloured salts of copper, iron, nickel and manganese.

When borax ($Na_2B_4O_7.10H_2O$) is heated, it fuses, loses water of crystallization and swells up into a white porous mass which then melts into a clear transparent glassy bead, composed of sodium metaborate and boric anhydride.

$$Na_2B_4O_7.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 \xrightarrow{\text{Red heat}} \underset{\text{(Glassy bead)}}{2NaBO_2 + B_2O_3}$$

**Table 8.5. Cobalt nitrate test**

| *Observation* | *Inference* | *Chemistry involved* |
|---|---|---|
| Blue residue | Aluminium salt | $2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$<br>$CoO+\underset{\text{(Al oxide in cavity)}}{Al_2O_3} \longrightarrow \underset{\text{(Blue residue)}}{Co(AlO_2)_2}$ |
| Pink residue | Magnesium salt | $2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$<br>$CoO+\underset{\text{(Mg oxide in cavity)}}{MgO} \longrightarrow \underset{\text{(Pink residue)}}{CoO.MgO}$ |
| Green residue | Zinc salt | $2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$<br>$CoO+\underset{\text{(Zn oxide in cavity)}}{ZnO} \longrightarrow \underset{\text{(Green residue)}}{CoZnO_2}$ |

When this bead is heated with coloured mixture, a characteristic coloured bead of metaborate (metal oxide from metal salt reacts with bead) is formed. Thus with copper salts a green metaborate (while hot) is obtained in the *oxidizing flame* :

$$CuSO_4 \longrightarrow CuO+SO_3$$

$$CuO+B_2O_3 \longrightarrow \underset{\substack{\text{Cupric metaborate}\\ \text{(Blue green)}}}{Cu(BO_2)_2}$$

In *reducing flame*, higher metaborates are reduced to lower metaborates or metal, consequently colour changes may occur. Thus in case of cupric metaborate the following changes occur in the *reducing flame*.

$$2Cu(BO_2)_2 + \underset{\substack{\text{(From reducing}\\ \text{flame)}}}{C} \longrightarrow \underset{\substack{\text{Cuprous metaborate}\\ \text{(Colourless)}}}{2CuBO_2} + B_2O_3+CO$$

$$2CuBO_2+C \longrightarrow \underset{\text{(Reddish)}}{2Cu} + B_2O_3+CO$$

**Procedure for a borax bead test.** Take a platinum wire and make a loop at the end of the wire. Heat the loop in flame and dip it into borax powder taken in a watch glass. Heat it again, when the borax swells up and then melts to form a colourless, transparent bead which fills the loop completely. If the bead is not colourless and transparent, jerk it off, and prepare the bead again. Now bring the hot bead in the cantact of a coloured salt and heat it again, first in oxidizing flame [Fig. 8.3 (*a*)] and then in a reducing flame [Fig. 8.3 (*b*)]. Note the colour of the bead in each case (hot and cold) and draw the inference (Table 8.6).

### Notes about borax bead test

1. Before touching the borax bead with the test salt or mixture, make sure that the bead is transparent and colourless. If it is

### Table 8.6. Borax-bead test

| *Observation* | | *Inference* | *Chemistry involved* |
|---|---|---|---|
| *In oxidizing flame* | *In reducing flame* | | |
| Green when hot blue when cold | — | Copper | $CuSO_4+B_2O_3 \longrightarrow Cu(BO_2)_2+SO_3$<br>(From bead) (Green when hot, blue when cold) |
| — | Colourless when hot red when cold | Copper | $2Cu(BO_2)_2+C \longrightarrow 2CuBO_2+B_2O_3+CO$<br>(Colourless when cold)<br>$2CuBO_2+C \longrightarrow 2Cu+B_2O_3+CO$<br>(Red when hot) |
| Reddish brown when hot, yellow when cold | Yellow when hot, green when cold | Iron | In both the types of flames $Fe(BO_2)_2$ is formed |
| Violet, hot or cold | Colourless, hot or cold | Manganese | In both the types of flames $Mn(BO_2)_2$ is formed |
| Brown, hot or cold | — | Nickel | $Ni(BO_2)_2$ is formed |
| — | Grey when cold | Nickel | Metallic nickel is obtained |

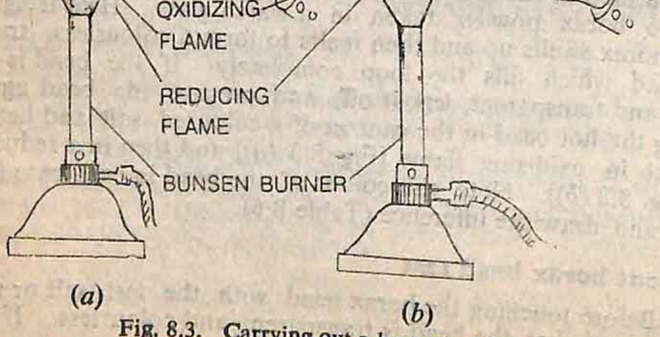


Fig. 8.3. Carrying out a borax-bead test.

coloured, the platinum wire is not clean. In such cases, jerk off the bead by a tap with your finger at the glass rod carrying wire. Prepare a fresh bead once again until it is colourless and transparent.

2. Do not perform this test with a colourless salt or mixture.

3. Always use a very small amount of the coloured salt or mixture.

4. The students should keep in mind that colour of the bead changes with temperature.

The physical examination and dry tests, thus, can help in identifying the anion and cation present in a given salt. However, it is essential that wet tests should be performed to confirm their presence. We shall now proceed with the identification of the anion present in the salt.

## 8.4. Detection of Anions

For identifying, the anions are divided into three groups :

(*i*) **Dilute sulphuric acid group.** This group includes carbonate ($CO_3^{2-}$), bicarbonate ($HCO_3^-$), sulphite ($SO_3^{2-}$), sulphide ($S^{2-}$) and nitrite ($NO_2^-$) anions.

(*ii*) **Concentrated sulphuric acid group.** This group includes chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), nitrate ($NO_3^-$) and acetate ($CH_3COO^-$) anions.

(*iii*) **A group not identified by dilute or concentrated sulphuric acid.** This includes sulphate ($SO_4^{2-}$) and phosphate ($PO_4^{3-}$) anions. They are identified by other reagents.

**Preparation of salt solution.** A salt solution is prepared for performing wet tests for anions. Some salts are very soluble in water, whereas others are partially soluble or totally insoluble in water. Thus, we may prepare the aqueous solution (called water extract) or sodium carbonate extract of the salt depending upon its solubility.

**Water extract.** All common nitrates, nitrites and many other salts are soluble in water.

Boil 1-2 g of the salt with 10-20 ml of distilled water for 5 min. If the salt dissolves completely, add more of it in small quantities to obtain a concentrated solution. If there is any suspension, filter the solution. This solution is known as water extract (we shall refer to it as W.E.)

**Sodium carbonate extract.** If the given salt is not completely soluble (insoluble) in water, its sodium carbonate extract is prepared.

Take 1-2 g of the salt and 4-8 g of sodium carbonate in a china dish. Add about 20 ml of distilled water and boil for about 20 min (Fig. 8.4*a*). Filter when hot (Fig. 8.4*b*). The filtrate thus obtained is called sodium carbonate extract (we shall refer to it as S.E.).

On boiling the salt with water and sodium carbonate, double decomposition take place forming carbonate of metallic part (insoluble) and sodium salt of the acid radical (soluble). For example, when insoluble barium phosphate salt is boiled with sodium carbonate solution, barium carbonate (insoluble) and sodium phosphate (soluble) are formed.

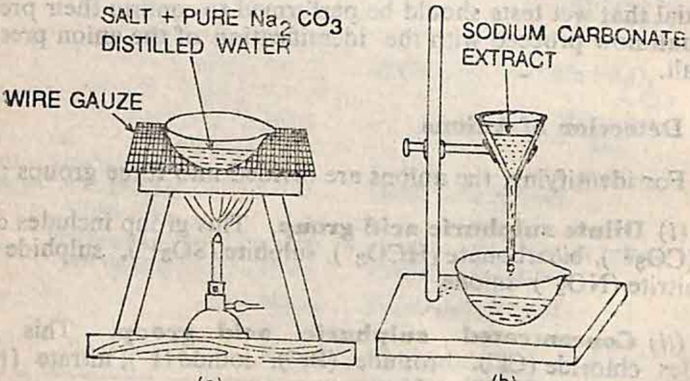


Fig. 8.4. Preparation of sodium carbonate extract.

$$Ba_3(PO_4)_2 + 3Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{3BaCO_3} + \underset{\text{(Soluble)}}{2Na_3(PO_4)_2}$$

Sodium carbonate extract contains an excess of unreacted sodium carbonate which interfere in the usual tests of anions. Thus, it is imperative to destroy the excess of sodium carbonate. This is accomplished by acidifying the extract. The choice of the acid depends upon the anion to be tested.

### Dilute sulphuric acid group

Treat the salt with dilute sulphuric acid (Table 8.7) and observe the reaction. This treatment will help us in finding out which one of the following anions is present : (*i*) carbonate, (*ii*) bicarbonate, (*iii*) sulphide, (*iv*) sulphite, and (*v*) nitrite.

## Table 8.7. Identification of $CO_3^{2-}$, $HCO_3^-$, $S^{2-}$, $SO_3^{2-}$ and $NO_2^-$

| | *Experiment* | *Observation* | *Inference* |
|---|---|---|---|
| 1. | Take a little of the salt in a test tube and add dil. $H_2SO_4$. Observe if any reaction takes place in cold. Warm gently and observe the gas. | (*i*) Brisk effervescence (due to evolution of $CO_2$) | $CO_3^{2-}$ or $HCO_3^-$ present |
| | | (*ii*) Rotten egg smelling gas (due to evolution of $H_2S$) | $S^{2-}$ present |
| | | (*iii*) Suffocating odour of burning sulphur (due to $SO_2$) | $SO_3^{2-}$ present |
| | | (*iv*) Light brown gas with punzent odour | $NO_2^-$ present |
| 2. | If there is brisk effervescence, pass the gas through lime water (Fig. 8.5) | Solution turns milky (due to the formation of $CaCO_3$) | $CO_3^{2-}$ confirmed |
| 3. | If a rotten egg smelling gas evolves, bring a piece of filter paper soaked in | | |
| | (*i*) acidified lead acetate solution near the gas | Paper turns black (due to formation PbS) | $S^{2-}$ confirmed |
| | (*ii*) acidified potassium permanganate near the gas | Violet colour decolourizes (due to formation of $MnSO_4$) and a yellow turbidity of S appears | $S^{2-}$ confirmed |
| | (*iii*) acidified potassium dichromate near the gas | Acquires light green colour (due to formation of $Cr_2(SO_4)_3$ and a yellow turbidity of S appears | $S^{2-}$ confirmed |
| 4. | To 1 ml of W.E. or S.E. add a few drops of sodium nitroprusside solution to which a few drops of alkali has been added | Violet or purple colour due to formation of $Na_4[Fe(CN)_5NOS]$ | $S^{2-}$ confirmed |
| 5. | Acidity 1 ml of S.E. with dilute acetic acid and add 1 ml of lead acetic solution | Black ppt. (due to formation of PbS) | $S^{2-}$ confirmed |
| 6. | Add 0·2 g of cadmium carbonate (powder) to 2 ml of S.E. and shake well. | Yellow ppt. of CdS is obtained | $S^{2-}$ confirmed |
| 7. | On treating the salt with dil. $H_2SO_4$, if there is suffocating odour of burning sulphur (pungent gas) bring a filter paper soaked in | | |
| | (*i*) acidified potassium permanganate near the gas | Violet colour decolourizes due to formation of $MnSO_4$ (colourless) | $SO_3^{2-}$ confirmed |

| | | |
|---|---|---|
| (*ii*) acidified potassium dichromate near the gas | Orange colour turns green due to formation of $Cr_2(SO_4)_3$ | $SO_3^{2-}$ confirmed |
| 8. Acidify 1 ml of S.E. with dilute acetic acid, boil off $CO_2$ gas and now add 1 ml of $BaCl_2$ solution. | A white ppt., soluble in dilute HCl is obtained ($BaSO_3$) | $SO_3^{-3}$ confirmed |
| 9. On treating the salt if brown gas evolves bring a small piece of filter paper dipped into starch+KI solution. | Paper turns blue due to the reactions of starch and $I_2$ | $NO_2^-$ confirmed |
| 10. Neutralize 1 ml of S.E. with acetic acid. Add of ≈0·2 g KCl+4 drops of cobalt chloride and warm. | On standing a yellow ppt. of $K_2Na[Co(NO_2)_6]$ is obtained. | $NO_2^-$ confirmed |

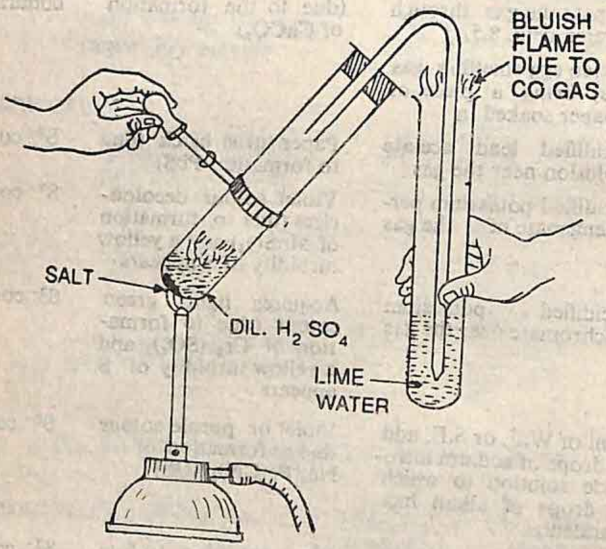


Fig. 8.5. Passing carbon dioxide through lime water.

## Distinction between carbonate and bicarbonate

Dissolve about 0·5 g of the salt in 4 ml of distilled water and divide it into 2 parts.

(*a*) To 1st part add a few drops of dil. HCl. A brisk effervescence due to evolution of $CO_2$ indicates, bicarbonate or carbonate.

$$Na_2CO_3 + 2HCl \longrightarrow H_2O + CO_2 + 2NaCl$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

(*b*) To 2nd part add 0·5 ml of $MgSO_4$ solution and shake well. Formation of a white ppt. in cold confirms the presence of soluble carbonate.

$$Mg^{2+} + CO_3^{2-} \longrightarrow \underset{\text{White ppt.}}{MgCO_3 \downarrow}$$

If no ppt. appears in cold, then heat to boiling Formation of a white ppt. confirms the presence of bicarbonate :

$$Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2$$

$$Mg(HCO_3)_2 \longrightarrow \underset{\text{(White ppt.)}}{MgCO_3 \downarrow} + H_2O + CO_2$$

The chemistry involved in the tests performed (Table 8.7) to identify $CO_3^{2-}$, $HCO_3^-$, $S^{2-}$, $SO_3^{2-}$ and $NO_2^-$ ions is outlined below :

**Reactions :**

1. (*i*) Carbonates and bicarbonates decompose on reacting with dilute sulphuric acid. Carbon dioxide gas evolves with brisk effervescence

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2(g)$$

$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2(g)$$

(*iii*) Sulphides react with dilute sulphuric acid and a rotten-egg smelling hydrogen sulphide gas evolves.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S(g)$$

(*iii*) Sulphites when react with dilute $H_2SO_4$ give suffocating odour of burning sulphur (pungent smelling sulphur dioxide gas).

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2(g)$$

(*iv*) Nitrites react with dilute $H_2SO_4$ giving brown coloured $NO_2$ gas

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + NO(g) + NO_2(g)$$

2. Lime water reacts with carbon dioxide gas and turns milky due to the formation of calcium carbonate.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{(Milky white)}}{CaCO_3(s)}$$

Precipitate of calcium carbonate reacts with more of carbon dioxide and milkiness disappears due to the formation of soluble calcium bicarbonate.

$$\underset{\text{(Insoluble)}}{CaCO_3(s)} + CO_2 \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2(aq)}$$

3. (*i*) Lead acetate paper acquires black colour on interacting with hydrogen sulphide gas. This is due to the formation of lead sulphide (black in colour).

$$(CH_3COO)_2Pb + H_2S \longrightarrow 2CH_3COOH + \underset{\text{(Black)}}{PbS(s)}$$

(*ii*) The violet colour of the potassium permanganate paper is discharged due to the formation of manganese (II) sulphate (colourless) and a yellow deposit appears. $KMnO_4$ oxidizes $H_2S$ to give S.

$$\underset{\text{(Violet)}}{2KMnO_4}+3H_2SO_4+5H_2S \longrightarrow K_2SO_4+\underset{\text{(Colourless)}}{2MnSO_4(aq)}+8H_2O+\underset{\text{(Yellow)}}{5S(s)}$$

(*iii*) Orange coloured potassium dichromate paper acquires a green colour due to the formation of chromium (III) sulphate (green) and a yellow deposit appears. $K_2Cr_2O_7$ oxidizes $H_2S$ to give S.

$$\underset{\text{(Orange)}}{K_2Cr_2O_7}+4H_2SO_4+3H_2S \longrightarrow K_2SO_4+\underset{\text{(Green)}}{Cr_2(SO_4)_3(aq)}$$
$$+7H_2O \;+\; \underset{\text{(Yellow)}}{3S(s)}$$

4. Sulphides react with sodium nitroprusside forming a violet coloured complex, $Na_4[Fe(CN)_5NOS]$.

$$Na_2S+\underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN_5)NO)} \longrightarrow \underset{\text{(Violet)}}{Na_4[Fe(CN)_5NOS](aq)}$$

5. Sulphides react with acidic lead acetate solution forming black precipitate of lead sulphide.

$$H_2S+(CH_3COO)_2Pb \longrightarrow 2CH_3COOH+\underset{\text{(Black)}}{PbS\ (s)}$$

6. Sulphides react with cadmium carbonate. A yellow precipitate of cadmium sulphide is obtained.

$$Na_2S+CdCO_3 \longrightarrow Na_2CO_3+\underset{\text{(Yellow)}}{CdS\ (s)}$$

7. (*i*) The violet colour of potassium permanganate paper is discharged on reacting with sulphur dioxide due to the formation of manganese (II) sulphate. Sulphur dioxide acts as a reducing agent.

$$2KMnO_4+3H_2SO_4 \longrightarrow K_2SO_4+2MnSO_4+3H_2O+5(O)$$
$$\underline{5SO_2+5H_2O+5(O) \longrightarrow 5H_2SO_4}$$
$$\underset{\text{(Violet)}}{2KMnO_4}+5SO_2+2H_2O \longrightarrow K_2SO_4+2H_2SO_4+\underset{\text{(Colourless)}}{2MnSO_4}$$

(*ii*) Orange coloured potassium dichromate paper acquires a light green colour on reacting with sulphur dioxide and due to the formation of $Cr_2(SO_4)_3$. Sulphur dioxide acts as an reducing agent.

$$\underset{\text{(Orange)}}{K_2Cr_2O_7}+H_2SO_4+3SO_2 \longrightarrow K_2SO_4+H_2O+\underset{\text{(Green)}}{Cr_2(SO_4)_3}$$

8. Sulphites react with barium chloride solution forming a white precipitate of barium sulphite. Barium sulphite is soluble in dilute hydrochloric acid.

$$Na_2CO_3+BaCl_2 \longrightarrow 2NaCl+\underset{\text{(White)}}{BaSO_3\ (s)}$$
$$BaSO_3+2HCl \longrightarrow BaCl_2+H_2O+SO_2$$

9. Starch-iodide paper turns blue due to the liberation of iodine from iodide by nitrous acid which reacts with starch.

$$KI+2HNO_2 \longrightarrow 2H_2O+2NO+\underset{\text{(From }NO_2^-\text{)}}{I_2}$$
$$I_2+\text{Starch} \longrightarrow \text{Blue colouration}$$

10. Nitrites react with cobalt chloride in the presence of acetic acid. A yellow crystalline precipitate of $K_2Na[Co(NO_2)_6]$ is formed,

$$6NaNO_2 + 2KCl + CoCl_3 \longrightarrow \underset{\text{(Yellow)}}{K_2Na[Co(NO_2)_6]\,(s)} + 5NaCl$$

**Concentrated sulphuric acid group**

Take about 0·5 g of the solid salt or mixture in a dry test-tube, add about 1 ml. of conc. $H_2SO_4$. Warm the contents (do not boil). Look for the presence of : (*i*) chloride, $Cl^-$, (*ii*) bromide, $Br^-$, (*iii*) iodide, $I^-$, (*iv*) nitrate, $NO_3^-$ and acetate, $CH_3COO^-$.

**Table 8.8. Identification of $Cl^-$, $Br^-$, $I^-$, $No^-_3$ and $CH_3COO^-$**

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| 1. Take a small quantity of the salt in a test-tube and add conc. $H_2SO_4$. Observe if any reaction takes place in cold. Warm gently and observe the gas evolved. | (*i*) Pungent smelling and irritating gas (due to evolution of HCl) | $Cl^-$ present |
| | (*ii*) Reddish brown fumes evolves (may be due to HBr and $Br_2$) | $Br^-$ present |
| | (*iii*) Violet vapours | $I^-$ present |
| | (*iv*) Light brown fumcs with a characteristic irritating smell (due to $NO_2$ gas) | $NO_3^-$ present |
| | (*v*) Vinegar smell | $CH_3COO^-$ present |
| 2. If a pungent smelling gas evolves | | |
| (*i*) bring a glass rod carrying a drop of ammonia solution near the issuing gas (Fig. 8.6) | Dense white fumes of $NH_4Cl$ are produced | $Cl^-$ present |
| (*ii*) add a small amount of $MnO_2$ to the reaction mixture and heat it. | Greenish yellow $Cl_2$ gas evolves. It has a pungent odour | $Cl^-$ present |
| (*iii*) Bring moist iodized starch-paper near the opening of the test-tube in (*ii*). | Dark blue colour appears. | $Cl^-$ present |
| 3. (*i*) Acidify 1 ml. of W.E. or S.E. with dilute $HNO_3$ and add $AgNO_3$ solution. | Dirty white ppt. of AgCl appears which turns grey on getting exposed to light | $Cl^-$ confirmed. |
| (*ii*) Add aqueous ammonia to the white ppt of AgCl. | ppt. dissolves forming a soluble complex | $Cl^-$ confirmed. |
| 4. **Chromyl Chloride Test :** Take a mixture of the salt (1 part) and $K_2Cr_2O_7$ (1 part) in a test tube. Add conc. $H_2SO_4$ and heat | Red vapours of chromyl chloride are produced. | $Cl^-$ confirmed |
| Pass the red vapours of $CrO_2Cl_2$ through dil. NaOH solution | Yellow solution of sodium chromate is obtained. | $Cl^-$ confirmed. |
| Acidify the yellow solution with acetic acid and add lead acetate solution. | Yellow ppt. of lead chromate is obtained | $Cl^-$ confirmed. |

| | | |
|---|---|---|
| 5. If a salt on treating with conc. $H_2SO_4$ produces brown fumes of HBr and $Br_2$ | | |
| (*i*) add a small quantity of $MnO_2$ to the reaction mixture and heat it | Dark brown fumes of $Br_2$ evolve | $Br^-$ present |
| (*ii*) Expose a starch paper to the issuing fumes | Starch paper turns yellow. | $Br^-$ present |
| 6. (*i*) Acidify 1 ml of W.E. or S.E. with dilute $HNO_3$ and add $AgNO_3$ solution | Light yellow curdid ppt. of AgBr | $Br^-$ confirmed. |
| (*ii*) Add aqueous ammonia solution to the yellow ppt. | Sparing soluble in ammonia solution | $Br^-$ confirmed. |
| 7. Acidify 1 ml of W.E. or S.E. with dilute $H_2SO_4$. Add 2 ml of an organic solvent ($CS_2$, $CHCl_3$, $CCl_4$ or benzene) followed by chlorine water. Shake the tube well. | Organic layer acquires yellow, red or brown colour depending on the concentration of $Br_2$ and on the solvent | $Br^-$ confirmed. |
| 8. If a salt on treating with conc. $H_2SO_4$ produces violet vapours of iodine | | |
| (*i*) add a small amount of $MnO_2$ to reaction mixture and heat | Dense violet vapours evolve | $I^-$ present |
| (*ii*) Expose a starch paper to the issuing vapours. | Starch paper turns blue. | $I^-$ confirmed. |
| 9. (*i*) Acidify 1 ml of W.E. or S.E. with dilute $HNO_3$ and add $AgNO_3$ solution. | Yellow curdid ppt. of AgI | $I^-$ confirmed. |
| (*ii*) Add aqueous ammonia solution to the yellow ppt. | Insoluble in aqueous ammonia | $I^-$ confirmed. |
| 10. Acidify 1 ml of W.E. or S.E. with dilute $H_2SO_4$. Add 2 ml of an organic solvent ($CS_2$, $CHCl_3$, $CCl_4$ or benzene) and about 1 ml of chlorine water. Shake well. | Organic layer extracts iodine and becomes red-violet. | $I^-$ confirmed. |
| 11. If a salt on reacting with conc. $H_2SO_4$ produces light brown fumes. | | |
| (*i*) add copper turnings to the reaction mixture and heat | Dense brown fumes evolve | $NO_3^-$ present |
| (*ii*) Expose a moist potassium iodide paper to the issuing fumes | The paper acquires yellow colour | $NO_3^-$ present |
| (*iii*) Expose a moist iodized starch paper to the issuing fumes. | The paper acquires a blue colour | $NO_3^-$ present |
| 12. To W.E. add freshly prepared ferrous sulphate solution followed by conc. $H_2SO_4$ along the side of the tube. | Conc. $H_2SO_4$ forms the bottom layer. A brown ring appears at the junction of the two liquids due to the formation of complex. | $NO_3^-$ confirmed. |

| | | |
|---|---|---|
| 13. If a salt on reacting with conc. $H_2SO_4$ gives vinegar smell, add a few ml of ethyl alcohol | Pleasant odour | $CH_3COO^-$ present |
| 14. To W.E. add neutral ferric chloride solution | Blood red coloured solution | $CH_3COO^-$ confirmed. |
| Heat the blood-red coloured solution | A red brown ppt. of basic acetate is precipitated | $CH_3COO^-$ confirmed. |

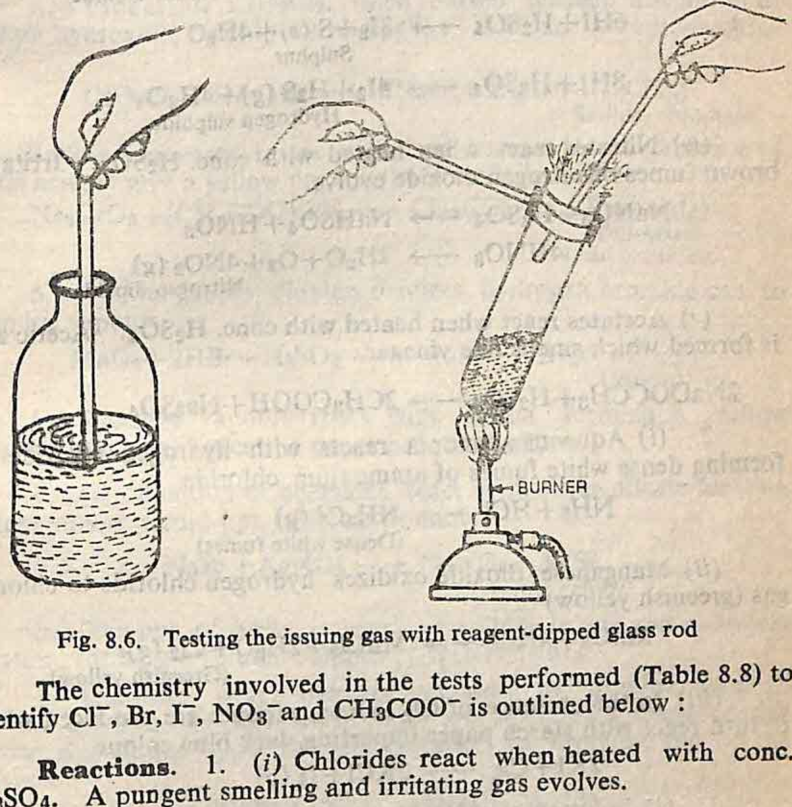


Fig. 8.6. Testing the issuing gas with reagent-dipped glass rod

The chemistry involved in the tests performed (Table 8.8) to identify $Cl^-$, Br, $I^-$, $NO_3^-$ and $CH_3COO^-$ is outlined below :

**Reactions.** 1. (*i*) Chlorides react when heated with conc. $H_2SO_4$. A pungent smelling and irritating gas evolves.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{hydrogen chloride}}{HCl\,(g)}$$

(*ii*) Bromides react when heated with conc. $H_2SO_4$. Reddish brown fumes evolve with a penetrating odour of a mixture of hydrogen bromide and bromine. $SO_2$ is also produced as HBr produced in reaction acts as reducing agent.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Hydrogen bromide}}{HBr\,(g)}$$

$$2HBr + H_2SO_4 \longrightarrow Br_2\,(g) + \underset{\text{Sulphur dioxide}}{SO_2(g)} + 2H_2O$$

(*iii*) Iodides react when heated with conc. $H_2SO_4$. Dense violet vapours evolve. Some hydrogen iodide gas also forms which reduces $H_2SO_4$ to $SO_2$, $H_2S$ and S.

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Hydrogen iodide}}{HI\,(g)}$$

$$2HI + H_2SO_4 \longrightarrow 2H_2O + I_2(g) + \underset{\text{Sulphur dioxide}}{SO_2\,(g)}$$

$$6HI + H_2SO_4 \longrightarrow 3I_2 + \underset{\text{Sulphur}}{S\,(s)} + 4H_2O$$

$$8HI + H_2SO_4 \longrightarrow 4I_2 + \underset{\text{Hydrogen sulphide}}{H_2S\,(g)} + 4H_2O$$

(*iv*) Nitrates react when heated with conc. $H_2SO_4$. Irritating brown fumes of nitrogen dioxide evolve.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow 2H_2O + O_2 + \underset{\text{Nitrogen dioxide}}{4NO_2\,(g)}$$

(*v*) Acetates react when heated with conc. $H_2SO_4$. Acetic acid is formed which smells like vinegar.

$$2NaOOCCH_3 + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$$

2. (*i*) Aqueous ammonia reacts with hydrogen chloride gas forming dense white fumes of ammonium chloride

$$NH_3 + HCl \longrightarrow \underset{\text{(Dense white fumes)}}{NH_4Cl\,(g)}$$

(*ii*) Manganese dioxide oxidizes hydrogen chloride to chlorine gas (greenish yellow)

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + \underset{\text{(Greenish yellow)}}{Cl_2\,(g)}$$

(*iii*) In the presence of $Cl_2$ iodine vapours are produced which in turn react with starch paper imparting dark blue colour.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2\,(g)$$

3. (*i*) Solution of chlorides react with silver nitrate forming a dirty white precipitate of silver chloride. It turns grey on getting exposed to light.

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{(Dirty white)}}{AgCl\,(s)}$$

(*ii*) The ppt. of AgCl dissolves in aqueous ammonia forming a soluble complex, $[Ag(NH_3)_2]Cl$.

$$AgCl + 2NH_3 \longrightarrow \underset{\text{Diammine silver chloride}}{[Ag(NH_3)_2]Cl\,(aq)}$$

4. A mixture of chloride and potassium dichromate with conc. $H_2SO_4$ give red vapours of chromyl chloride, $CrO_2Cl_2$

$$\mathrm{4NaCl+K_2Cr_2O_7+3H_2SO_4 \xrightarrow{Heat} K_2SO_4+2Na_2SO_4+3H_2O} + \underset{\substack{\text{(Red vapour)}\\ \text{Chromyl chloride}}}{\mathrm{2CrO_2Cl_2}\,(g)}$$

Red vapours of $CrO_2Cl_2$, when passed through a solution of sodium hydroxide, react to form a yellow solution of sodium chromate

$$\mathrm{CrO_2Cl_2+4NaOH \longrightarrow 2NaCl+2H_2O+}\underset{\text{Sodium chromate}}{\mathrm{Na_2CrO_4}}$$

Sodium chromate reacts with lead acetate in the presence of acetic acid to give a yellow precipitate of lead chromate.

$$\mathrm{Na_2CrO_4+(CH_3COO)_2Pb \longrightarrow CH_3COONa+}\underset{\substack{\text{(Yellows)}\\ \text{Lead chromate}}}{\mathrm{PbCrO_4}(s)}$$

5. (*i*) Manganese dioxide oxidizes hydrogen bromide gas to bromine vapours.

$$\mathrm{MnO_2+2HBr+H_2SO_4 \longrightarrow MnSO_4+2H_2O+}\underset{\text{(Brown)}}{\mathrm{Br_2}(g)}$$

(*ii*) Bromine vapours react with starch forming a yellow coloured complex, hence the paper becomes yellow.

6. (*i*) Solution of bromides react with silver nitrate forming a light yellow curdid ppt. of silver bromide.

$$\mathrm{NaBr+AgNO_3 \longrightarrow NaNO_3+}\underset{\text{(Light yellow)}}{\mathrm{AgBr}}$$

(*ii*) The ppt. of AgBr is sparingly soluble in aqueous ammonia solution, forming a soluble complex, $[Ag(NH_3)_2]Br_2$.

7. Chlorine water oxidizes bromides to bromine. Organic solvent extracts the liberated bromine and acquires a yellow orange colour depending upon the concentration of bromine and on the solvent.

$$\mathrm{2NaBr+Cl_2 \longrightarrow 2NaCl} + \underset{\substack{\text{(Soluble in organic}\\ \text{solvent)}}}{\mathrm{Br_2}}$$

8. (*i*) Hydrogen iodide is readily oxidized to iodine by manganese dioxide when more of violet vapours of iodine evolve.

$$\mathrm{MnO_2+2HI+H_2SO_4 \longrightarrow MnSO_4+2H_2O} + \underset{\text{(Violet)}}{\mathrm{I_2}(g)}$$

(*ii*) Iodine vapours react with starch forming a blue coloured complex ; hence the paper becomes blue.

9. (*i*) Solution of iodides react with silver nitrate to give a yellow curdid precipitate of silver iodide.

$$\mathrm{NaI+AgNO_3 \longrightarrow NaNO_3+}\underset{\text{(Yellow)}}{\mathrm{AgI}(s)}$$

(*ii*) The precipitate of AgI is insoluble in aqueous ammonia.

10. Chlorine water oxidizes iodides to iodine. Organic solvent extracts the liberated iodine and acquires red violet colour.

$$2NaI+Cl_2 \longrightarrow 2NaCl + \underset{\text{(Soluble in organic solvent)}}{I_2}$$

11. (*i*) Copper turnings react with nitric acid produced in the reaction mixture forming more of nitrogen dioxide, hence the dense brown fumes.

$$NaNO_3+H_2SO_4 \longrightarrow HNO_3+NaHSO_4$$

$$Cu+4HNO_3 \longrightarrow Cu(NO_3)_2+2H_2O+\underset{\substack{\text{(Brown)}\\ \text{Nitrogen dioxide}}}{2NO_2(g)}$$

(*ii*) Iodine liberates during the reaction and the paper absorbs iodine which imparts yellow colour.

$$NO_2+2KI+H_2O \longrightarrow 2KOH+NO+I_2(g)$$

(*iii*) Iodine liberates during the reaction and it interacts with starch forming a blue coloured complex.

12. Nitrates react with ferrous sulphate in the presence of conc. $H_2SO_4$. A brown ring appears at the junction of the two liquid layers (Fig. 8.7).

Ferrous sulphate, at first, reduces the nitrate to nitrite and then to nitric oxide. This oxide coordinates to the unoxidized portion of ferrous sulphate.

$$NO_3^-+H^+ \longrightarrow HNO_3$$

$$2HNO_3+3H_2SO_4+6FeSO_4 \longrightarrow 3Fe_2(SO_4)_2 +2NO+4H_2O$$

$$FeSO_4+5H_2O+NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]SO_4}$$

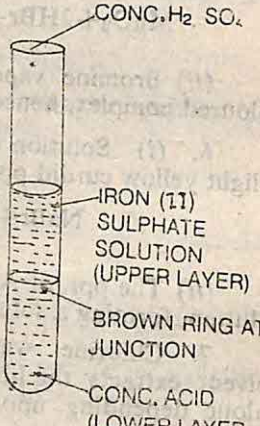


Fig. 8.7. Brown ring test for nitrate.

13. Acetic acid and its salt form, under the action of ethyl alcohol in the presence of sulphuric acid, form ethyl acetate which is detected by its pleasant odour.

$$CH_3COOH^++HOC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} CH_3COOC_2H_5+H_2O$$

14. Ferric salts with acetate ions form ferric acetate which is recognized by its blood-red colour.

$$3CH_3COONa+FeCl_3 \longrightarrow \underset{\text{(Blood-red)}}{(CH_3COO)_3Fe}+3NaCl$$

On dilution and heating, basic acetate is precipitated.

$$(CH_3COO)_3Fe+2H_2O \longrightarrow \underset{\text{Basic acetate}}{[CH_3COO(OH)_2]Fe(s)}+2CH_3COOH$$

**Tests for anions not identified by dilute or concentrated $H_2SO_4$**

Anion which cannot be identified on reacting with dilute or conc. $H_2SO_4$, are listed below.

(*i*) Sulphate, $SO_4^{2-}$ ; and (*ii*) phosphate ; $SO_4^{3-}$.

Such anoins are identified and thus confirmed by using sodium carbonate exract only. Some other tests can also be performed.

Proceed as given in Table 8.9.

**Table 8.9. Identification of $SO_4^{2-}$, and $PO_4^{3-}$**

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| 1. Acidify 2-3 ml of W.E. or S.E. with dil. HCl and divide the solution in two parts. | | |
| (*i*) To one part add barium chloride solution. | White ppt. of $BaSO_4$ is obtained. Insoluble in all mineral acids. | $SO_4^{2-}$ confirmed |
| (*ii*) To the other part of the solution add acetic acid and lead acetate solution | White ppt. of lead sulphate is obtained which is soluble in ammonium acctate solution, due to the formation of soluble lead acetate. | $SO_4^{2-}$ confirmed |
| 2. Acidify 2-3 ml of S.E. with dil. $HNO_3$. To this add 2-3 ml of conc. $HNO_3$ and 5 ml of ammonium molybdate solution. Now heat the contents. | Slow formation of canary-yellow ppt. of ammonium phosphomolybdate takes place. | $PO_4^{-3}$ present |

The chemistry involved in the tests performed (Table 8.9) to identify $SO_4^{2-}$ and $PO_4^{3-}$ is outlined below :

**Reactions**

1. (*i*) Solutions of sulphates react with barium chloride and form a white precipitate of barium sulphate which is insoluble in all mineral acids.

$$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + \underset{\text{(White)}}{BaSO_4(s)}$$

(*ii*) Solution of sulphates react with lead acetate and form a white precipitate of lead sulphate.

$$Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow 2CH_3COONa + \underset{\text{(White)}}{PbSO_4(s)}$$

Precipitate of lead sulphate dissolves in ammonium acetate solution due to the formation of soluble lead acetate.

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2SO_4 + \underset{\text{Lead acetate}}{(CH_3COO)_2Pb}$$

2. Solutions of phosphates react with ammonium molybdate in the presence of concentrated nitric acid to yield a canary-yellow precipitate of ammonium phosphomolybdate.

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 \longrightarrow \underset{\text{(Canary yellow)}}{(NH_4)_3[PMo_{12}O_{40}](s)}$$
$$+ 2NaNO_3 + 12NH_4NO_3 + 12H_2O$$

## 8.5. Detection of Cations

Cations are divided into analytical groups. The classification of the cations into analytical groups is based on the solubility of some salts which they form on reacting with reagents. All cations have been divided into six analytical groups on the basis of the difference in solubilities of their chlorides, sulphides, hydrnxides and carbonates under different conditions of acidity and alkalinity (Table 8.10). The reagent used to precipitate the specific group is known as a group reagent.

**Table 8.10. Classification of cations into groups**

| *Group* | *Group reagent* | *Cations* |
|---|---|---|
| I | Dilute HCl | $Pb^{2+}$ and $Hg_2^{2+}$(precipatated as chloride) |
| II | $H_2S$ in acidic medium (HCl) | $Hg^{2+}$, $Cu^{2+}$, $Cd^{2+}$ $As^{3+}$ and $Sb^{3+}$ (precipiteted as sulphides) |
| III | $NH_4OH$ in the presence of $NH_4Cl$ | $Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$ (precipitated as hydroxides) |
| IV | $H_2S$ in alkaline medium ($NH_4OH$) | $Ni^{2+}$, $Zn^{2+}$ $Mn^{2+}$ and $CO^{2+}$ (precipitated as sulphides) |
| V | $(NH_4)_2CO_2$ in alkaline medium ($NH_4OH$) | $Ca^{2+}$, $Ba^{2+}$ and $Sr^{2+}$ (precipitated as carbonates) |
| VI | No common reagent | $Mg^{2+}$, $NH_4^+$, $K^+$ and $Na^+$ |

**Preparation of original solution**. Most of the reactions used in qualitative analysis occur in aqueous solution. Thus, the first step in the systematic analysis of cations is to prepare a clear (colourless or coloured) salt solution (called *original solution*, O.S.). For this purpose, take about 0·1 g of the salt and try to dissolve it in about 2 ml of

(*i*) distilled water (cold or hot),

(*ii*) dilute hydrochloric acid (cold or hot), or

(*iii*) concentrated hydrochloric acid (cold or hot).

The solvents listed above should be tried one by one in the given order. After selecting the suitable solvent, prepare the O.S. by dissolving about 1 g of the salt in 10-15 ml of the solvent.

**Notes.** (*i*) For the preparation of O.S. first try to dissolve the salt in a cold solvent (water, dilute hydrochloric acid or concentrated hydrochloric acid). If it does not dissolve, heat it. In such a case, cool the solution and see if the salt separates out or not. If it does, try the next solvent.

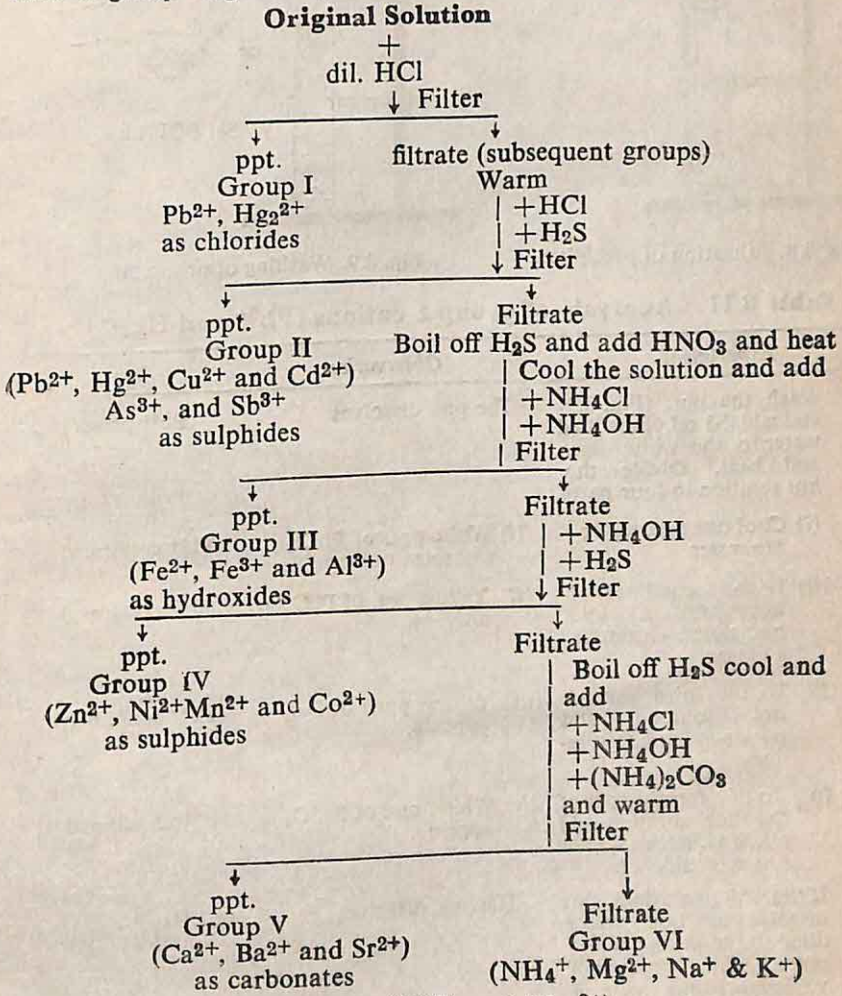
(*ii*) If the solution is prepared in concentrated hydrochloric acid, it should be diluted before proceeding with the cation analysis.

(*iii*) The effect of the solvent on the salt should be for a sufficient period.

(*iv*) The least quantity of the acid should be used for the preparation of original solution.

(*v*) At this level, it is advised not to employ $HNO_3$ and $H_2SO_4$ as solvent, as they interfere in the usual analysis. Sulphuric acid precipitates $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$ and $Pb^{2+}$ as their sulphates and thus salt containing these cations will never dissolve.

The classification and separation of all the six groups on the basis of group reagents is portrayed in the flow chart.



**Analysis of Group I Cations, ($Pb^{2+}$ and $Hg_2^{2+}$)**

Take about 10 ml of the *aqueous original solution*, and add a slight excess of dilute HCl. Formation of a white precipitate indicates the presence of group I. Filter the precipitate (Fig. 8.8). Keep the filtrate for the analysis of the subsequent groups. Analyze the ppt. for the cations of first group as given in the Table 8.11.

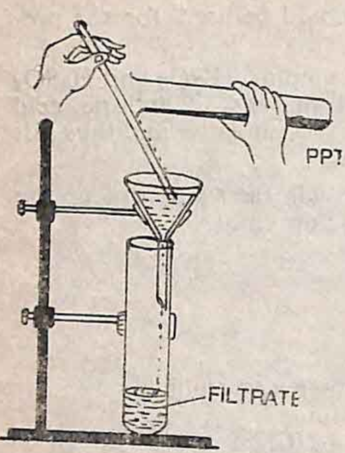


Fig. 8.8. Filtration of precipitate

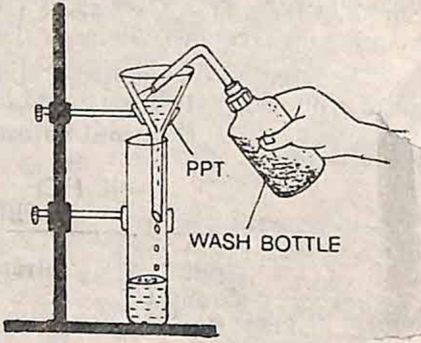


Fig. 8.9. Washing of precipitate

**Table 8.11. Analysis of group I cations ($Pb^{2+}$ and $Hg_2^{2+}$)**

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| 1. Wash the ppt. (Fig. 8.9) and add 2-3 ml of distilled water to the white ppt. and heat. Divide the hot solution in four parts. | The ppt. dissolves | $Pb^{2+}$ present |
| (*i*) Cool one part under tap water | (*i*) White ppt. of $PbCl_2$ separates out. | $Pb^{3+}$ confirmed |
| (*ii*) To the second part of hot solution add potassium chromate solution. | (*ii*) Yellow ppt. of $PbCrO_4$ appears. | $Pb^{2+}$ confirmed |
| (*iii*) To the third part of hot solution add potassium iodide solution. | (*iii*) Yellow ppt. of $PbI_2$ appears. | $Pb^{2+}$ confirmed |
| (*iv*) To the fourth part of the hot solution add dilute $H_2SO_4$ and a few drops of alcohol. | (*iv*) White ppt. of $PbSO_4$ appears. | $Pb^{2+}$ confirmed |
| 2. If the white ppt. does not dissolve in hot water filter and treat the white ppt. with minimum volume of aqua regia (1 part conc. $HNO_3$ and 3 parts conc. HCl) Heat to dryness. Treat the solid mass with water. Divide the solution in two parts | The ppt. dissolves | $Hg_2^{2+}$ present |

| | | |
|---|---|---|
| (*i*) To one part of the solution add KI solution | Red ppt. of $HgI_2$ appears | $Hg_2^{+2}$ confirmed |
| (The reaction should be carried out at $pH \leqslant 7$) | Red ppt. dissolves forming a complex | |
| Add excess of KI solution | | |
| (*ii*) To the other part of the solution add an equal volume of freshly prepared $SnCl_2$ solution | A white ppt. appears.<br>At times, a block ppt. appears | $Hg_2^{2+}$ confirmed |

**Notes.** (*i*) If the O.S. is prepared in dilute hydrochloric acid (cold) group I is absent. Proceed directly for the subsequent groups.

(*ii*) If the O.S. is prepared in concentrated hydrochloric acid, dilute the solution. If the precipitate appears on dilution, analyze it for the presence of lead (Group I).

The chemistry involved in the tests performed (Table 8.11) to identify $Pb^{2+}$ and $Hg_2^{2+}$ is outlined below :

**Reactions**

1. Lead salt solution on reacting with dilute hyhrochloric acid forms white precipitate of lead chloride which is soluble in hot water.

$$Pb^{2+} + 2HCl \longrightarrow \underset{\text{(White)}}{PbCl_2 \downarrow} + 2H^+$$

(*i*) Lead chloride appears on cooling the solution under tap water.

(*ii*) Lead salt solution reacts with potassium chromate to give yellow ppt. of lead chromate

$$\underset{\text{(Soluble in hot water)}}{PbCl_2\,(aq)} + K_2CrO_4 \longrightarrow \underset{\text{(Yellow)}}{PbCrO_4\,(s)} + 2KCl$$

(*iii*) Potassium iodide reacts with lead chloride solution forming a yellow ppt. of lead iodide.

$$PbCl_2\,(aq) + 2KI \longrightarrow 2KCl + \underset{\text{(Yellow)}}{PbI_2(s)}$$

The precipitate of lead iodide is soluble in hot solution, which reappears on cooling with a distinct shine.

(*iv*) Sulphate ions react with lead salt solution and form white ppt. (alcohol reduces the solubility of the ppt.) which is soluble in ammonium acetate solution

$$PbCl_2(aq) + H_2SO_4 \longrightarrow PbSO_4(s) + 2HCl$$

$$PbSO_4(s) + NH_4OOCCH_3 \longrightarrow (NH_4)_2\,SO_4 + PbOOCCH_3(aq)$$

2. Aqua regia dissolves the ppt. forming soluble mercuric chloride

$$Hg_2Cl_2 + 2HNO_3 + 6HCl \longrightarrow 2HgCl_2 + 2NaCl + 4H_2O + Cl_2$$

(*i*) Mercury salt solution reacts with KI solution. A red ppt. of $HgI_2$ appears.

$$Hg^{2+} + 2I^- \longrightarrow \underset{\text{(Red)}}{HgI_2(s)}$$

The red ppt. dissolves in the presence of excess reagent.

$$HgI_2 + 2I^- \longrightarrow \underset{\text{(Soluble)}}{[HgI_4]^{2-}}$$

(*ii*) Addition of $SnCl_2$ reduces $HgCl_2$ to white $Hg_2Cl_2$. The reaction is possible in acidic solution.

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{(White)}}{Hg_2Cl_2(s)} + SnCl_4$$

Further addition of $SnCl_2$ reduces white $Hg_2Cl_2$ to a black precipitate of metallic mercury

$$SnCl_2 + Hg_2Cl_2 \longrightarrow \underset{\text{(Black)}}{2Hg(s)} + SnCl_4$$

**Analysis of Group II Cations ($Pb^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $As^{3+}$ and $Sb^{3+}$)**

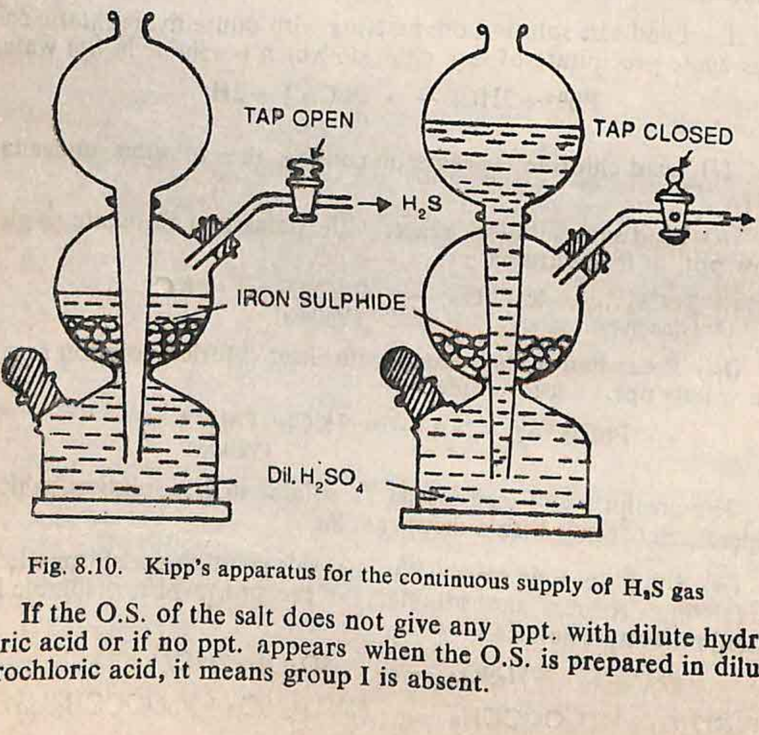


Fig. 8.10. Kipp's apparatus for the continuous supply of $H_2S$ gas

If the O.S. of the salt does not give any ppt. with dilute hydrochloric acid or if no ppt. appears when the O.S. is prepared in dilute hydrochloric acid, it means group I is absent.

Now warm this acidified O.S. and pass hydrogen sulphide gas from the Kipp's apparatus (Fig. 8.10) through the solution. If a coloured ppt. (black, yellow or orange) isobtained the group II appears to be present. A black ppt. shows the presence of $Pb^{2+}$, $Hg^{2+}$ or $Cu^{2+}$, a yellow ppt. shows $Cd^{2+}$ or $As^{3+}$ and a orange, ppt. shows $Sb^{3+}$. It is advisable to pass $H_2S$ gas through a few ml of O.S. initially. If there is ppt. then pass $H_2S$ gas through the remaining solution also. If there is no ppt. then reject this solution.

Now separate the ppt. by filtration and reject the filtrate.

$$Pb^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{PbS\,(s)} + 2H^+$$

$$Hg^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{HgS} + 2H^+$$

$$Cu^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{CuS\,(s)} + 2H^+$$

$$Cd^{2+} + H_2S \longrightarrow \underset{\text{(Yellow)}}{CdS\,(s)} + 2H^+$$

(Possible in very dilute solution only)

$$2As^{3+} + 3H_2S \longrightarrow \underset{\text{(Yellow)}}{As_2S_3\,(s)} + 6H^+$$

$$2Sb^{3+} + 3H_2S \longrightarrow \underset{\text{(Orange)}}{Sb_2S_3\,(s)} + 6H^+$$

**Table 8.12. Analysis of group II cations ($Pb^{2+}$, $Hg^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $As^{3+}$ and $Sb^{3+}$)**

Wash the ppt. with hot distilled water and reject the washings. Take the washed ppt. in a test tube (Fig. 8.11).

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| **Black ppt.** | | |
| 1. Treat the washed black ppt. with 3-4 ml of 50% $HNO_3$ and boil | A colourless or blue coloured solution is obtained | $Pb^{3+}$ or $Cu^{2+}$ indicated |
| 2. To the colourless solution (From test 1) add 1 ml of alcohol and a few ml of dil. $H_2SO_4$ | White ppt. (due to $PbSO_4$) | $Pb^{2+}$ present |
| To the white ppt. add ammonium acetate solution. | $PbSO_4$ is soluble in ammonium acetate solution | $Pb^{2+}$ present |
| Note. Divide the solution in two parts and perform the tests with $K_2CrO_4$, and KI as given in Table 8.11. | | |
| 3. To the blue solution (From test 1) add an excess of aqueous ammonia solution | A deep blue solution of $[Cu(NH_3)_4](NO_3)_2$ is obtained. | $Cu^{2+}$ confirmed |
| 4. To the O.S. (or the solution obtained in test no. 3) add potassium ferrocyanide solution | Reddish brown ppt. of $Cu_2[Fe(CN)_6]$ appears | $Cu^{2+}$ confirmed |

| | | |
|---|---|---|
| 5. Treat the black residue (From test 1) with aqua regia. Heat to almost dryness. Extract the solid mass in distilled water. Divide the solution in three parts. | | |
| **Note.** Perform the test with KI. and $SnCl_2$ as given in Table 8.12. | | |
| To the third part add Cu turnings | Grey deposit is seen on Cu | $Hg^{2+}$ confirmed. |
| **Yellow ppt.** | | |
| 6. Take the washed yellow ppt. in a test tube and boil it with 2-3 ml of yellow ammonium sulphide. | Yellow ppt. remains insoluble | $Cd^{2+}$ indicated |
| 7. Treat the yellow ppt. with 50% $HNO_3$ and warm. | Yellow ppt. is soluble and a solution of $Cd(NO_3)_2$ is obtained | $Cd^{2+}$ indicated |
| Divide the solution in two parts | | |
| (*i*) To one part of the solution add aqueous ammonia solution followed by excess of ammonia solution. | A white ppt, of $Cd(OH)_2$ is formed, which dissolves in excess of ammonia | $Cd^{3+}$ confirmed |
| Pass $H_2S$ through the solution. | Yellow ppt. of CdS | $Cd^{2+}$ confirmed |
| (*ii*) To the other part of the solution add $K_4[Fe(CN)_6]$ | A bluish white ppt. is formed | $Cd^{2+}$ confirmed |
| 8. (*i*) Take the washed yellow ppt. and boil it with yellow ammonium sulphide solution (as given in test 6). | Yellow ppt. dissolves forming soluble ammonium thioarsenate | $As^{3+}$ indicated |
| (*ii*) To the solution add dilute HCl | Yellow ppt. of $As_2S_3$ is obtained | $As^{3+}$ confirmed |
| 9. Dissolve the ppt. obtained in test 8 in conc. $HNO_3$. To this solution or to the O.S. add 2-3 ml of conc. $HNO_3$ and ammonium molybdate solution. Boil the mixed solution. | Yellow ppt. of ammonium arsenomolybdate is obtained | $As^{3+}$ confirmed |
| **Orange ppt.** | | |
| 10. (*i*) Take the washed orange ppt. in a test tube and boil it with yellow ammonium sulphide (as given in test 6) | Orange ppt. dissolves forming soluble ammonium thioantimonate | $Sb^{3+}$ indicated |
| (*ii*) Acidify the solution with dilute HCl | Orange ppt. is obtained | $Sb^{3+}$ confirmed |
| 11. Boil the ppt. obtained in test 10 with 5 ml conc. HCl for 5 min. and pass $H_2S$ gas through the hot solution. | Orange ppt. is obtained | $Sb^{3+}$ confirmed |

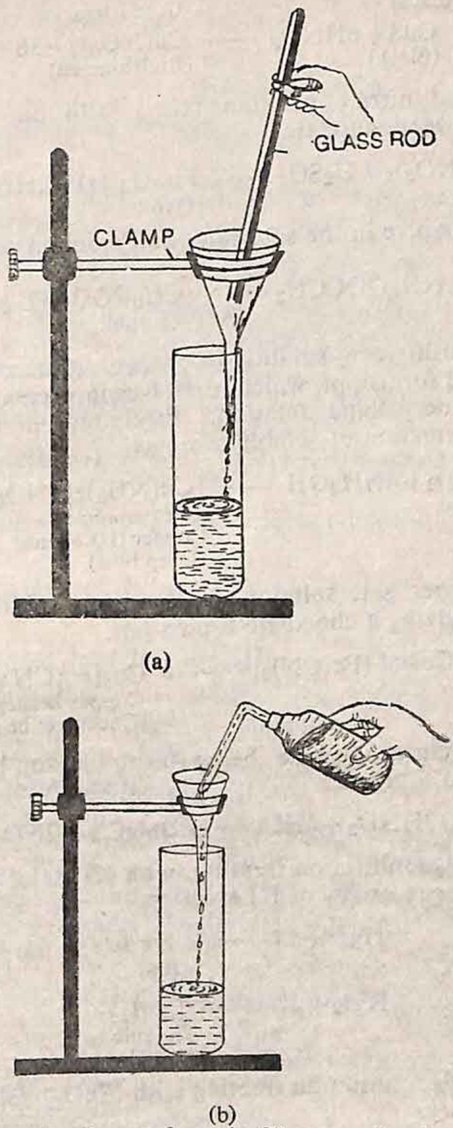


Fig. 8.11. (a) Removing the ppt. from the filter paper by piercing a hole in the filter paper, and (b) washing down it with a liquid from wash bottle.

The chemistry underlying the tests performed (Table 8.12) to identify $Pb^{2+}$, $Hg^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $As^{3+}$ and $Sb^{3+}$ is outlined below :

**Reactions**

1. Sulphides of lead and copper dissolve in nitric acid to give a colourless solution of lead nitrate and bluish green solution of copper nitrate. Sulphur is precipitated.

$$\underset{\text{(Black)}}{3PbS}+8HNO_3 \longrightarrow \underset{\text{(Colourless)}}{Pb(NO_3)_2}+3S+2NO+4H_2O$$

$$\underset{\text{(Black)}}{CuS}+8HNO_3 \longrightarrow \underset{\text{(Bluish-green)}}{Cu(NO_3)_2}+3S+2NO+4H_2O$$

2. Lead nitrate solution reacts with dil. $H_2SO_4$ forming a white ppt. of lead sulphate

$$Pb(NO_3)_2+H_2SO_4 \longrightarrow \underset{\text{(White)}}{PbSO_4}\,(s)+2HNO_3$$

which can dissolve in the solution of ammonium acetate.

$$PbSO_4+2NH_4OOCCH_3 \longrightarrow \underset{\text{(Soluble)}}{(CH_3COO)_2Pb}+(NH_4)_2SO_4$$

3. Bluish-green solution of copper nitrate reacts with aqueous ammonia and forms ppt. which dissolves in excess of ammonia solution giving a deep blue solution. Precipitate of $Cu(OH)_2$ dissolves due to the formation of soluble complex.

$$Cu(NO_3)_2+4NH_4OH \longrightarrow \underset{\substack{\text{Tetra-ammine}\\ \text{Copper (II) nitrate}\\ \text{(Deep blue)}}}{[Cu(NH_3)_4]\,(NO_3)_2}+4H_2O$$

4. Copper salt solution reacts with a solution of potassium ferrocyanide giving a chocolate brown ppt.

$$2Cu^{2+}+[Fe(CN)_6]^{4-} \longrightarrow \underset{\substack{\text{Copper hexacyanoferrate (II)}\\ \text{(Chocolate brown)}}}{Cu_2[Fe(CN)_6]}$$

5. Mercuric sulphide being insoluble, on heating with aqua regia goes into solution.

$$3HgS+2HNO_3+6HCl \longrightarrow 3HgCl_2+2NO+3S+4H_2O$$

(*i*) $HgCl_2$ solution on treating with KI solution gives red ppt. which dissolves in excess of KI solution.

$$Hg^{2+}+2I^- \longrightarrow \underset{\text{Red}}{Hg\,I_2(s)}$$

$$HgI_2+2I^- \longrightarrow \underset{\substack{\text{Soluble}\\ \text{complex}}}{[HgI_4]^{2-}}$$

(*ii*) $HgCl_2$ solution on treating with $SnCl_2$ solution reduces to metallic mercury.

$$2HgCl_2+SnCl_2 \longrightarrow \underset{\text{(While ppt.)}}{Hg_2Cl_2}+SnCl_4$$

$$Hg_2Cl_2+SnCl_2 \longrightarrow \underset{\text{(Black)}}{2Hg}+SnCl_4$$

(*iii*) On adding Cu turnings $HgCl_2$ is reduced to Hg which is deposited on copper. Displacement reaction takes place.

$$HgCl_2 + Cu \longrightarrow \underset{\text{(Deposited on Cu)}}{CuCl_2 + Hg}$$

6. Cadmium sulphide does not dissolve in ammonium sulphide.

7. Sulphide of cadmium dissolves in nitric acid forming soluble cadmium nitrate.

$$3CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O$$

(*i*) Addition of ammonia solution containing $Cd^{2+}$ ions causes precipitation of hydroxide of $Cd^{2+}$ which dissolves in excess of ammonia solution forming complex ion $[Cd(NH_3)_4]^{2+}$

$$Cd^{2+} + 2NH_4OH \longrightarrow \underset{\text{(White ppt.)}}{Cd(OH)_2\,(s)} + 2NH_4^+$$

$$Cd(OH)_2 + 4NH_4OH \longrightarrow \underset{\text{(Soluble complex)}}{[Cd(NH_3)_4]^{2+}} + 4H_2O + 2OH^-$$

When $H_2S$ is passed through the soluble complex, a yellow ppt. of CdS is obtained.

$$[Cd(NH_3)_4]^{2+} + H_2S \longrightarrow \underset{\text{(Yellow)}}{CdS\,(s)} + 2NH_4^+ + 2NH_3$$

(*ii*) Addition of $K_4[Fe(CN)_6]$ solution forms bluish white ppt.

$$2Cd^{2+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\text{(Bluish white)}}{Cd_2[Fe(CN)_6](s)}$$

8. (*i*) Yellow ppt. of $As_2S_3$ dissolves in yellow ammonium sulphide forming a soluble thiosalt.

$$\underset{\text{(Yellow)}}{As_2S_3} + 3(NH_4)_2S + 2S \longrightarrow \underset{\text{(Ammonium thioarsenate)}}{2(NH_4)_3AsS_4(aq)}$$

(*ii*) Acidification of ammonium sulphide extract containing thiosalts of $As^{3+}$ precipitates arsenic (V) sulphide. Some sulphur is also precipitated.

$$2(NH_4)_3AsS_4 + 6HCl \longrightarrow 6NH_4Cl + 3H_2S + \underset{\text{(Yellow)}}{As_2S_5(s)}$$

9. Nitric acid reacts with $As_2S_5$ and forms soluble $H_3AsO_4$ (arsenic acid). Arsenic salt on reacting with conc. nitric acid is oxidized to arsenic acid.

Arsenic acid solution reacts with ammonium molybdate forming a yellow ppt. of arsenomobyldate.

$$3As_2S_5 + 10HNO_3 + 4H_2O \longrightarrow \underset{\text{Arsenic acid}}{6H_3AsO_4} + 10NO + 15S$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{(Yellow)}}{(NH_4)_3[AsMo_{12}O_{40}](s)} + 21NH_4NO_3 + 12H_2O$$

**Note**. Phosphate, if present, also gives a similar test (tests). $As^{3+}$ should be confirmed by this test only if $PO_4^{3-}$ is absent in the salt.

10. (*i*) Orange ppt. of $Sb_2S_3$ dissolves in hot yellow ammonium sulphide forming a soluble thiosalt.

$$\underset{\text{(Orange)}}{Sb_2S_3}+3NH_4S+2S \longrightarrow \underset{\text{(Ammonium thioantimonate)}}{2(NH_4)_3SbS_4(aq)}$$

(*ii*) Acidification of ammonium sulphide extract containing thiosalt of $Sb^{3+}$ precipitates antimony (V) sulphide. Some sulphur is also precipitated.

$$2(NH_4)_3SbS_4+6HCl \longrightarrow \underset{\text{(Orange)}}{Sb_2S_5(s)}+6NH_4Cl+3H_2S$$

11. $Sb_2S_5$ dissolves in conc. HCl

$$Sb_2S_5+6HCl \longrightarrow SbCl_3(aq)+2S+3H_2S$$

Now on passing $H_2S$ gas through the solution antimony is precipitated as $Sb_2S_3$ which is identified by its characteristic orange colour.

## Analysis of Group III Cations ($Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$)

In case the cations of groups I and II are absent, proceed for identifying the cations of group III. To do this take 2-3 ml of O.S. or take the solution of group II (when group II is absent) and boil for sufficient time to remove $H_2S$ completely and also concentrate the solution to 5 ml. Add about 0·5 ml. of conc. $HNO_3$* and boil to oxidize $Fe^{2+}$ to $Fe^{3+}$. Oxidation is necessary otherwise precipitation of iron will be incomplete. Now to this add 0·5 g of solid $NH_4Cl$, followed by aqueous ammonia solution until the solution distinctly smells of ammonia. The formation of a precipitate indicates the presence of group III. Filter the precipitate and analyze the ppt. of the group III as given in the Table 8.13. Reject the filtrate.

$$3Fe^{2+}+NO_3^-+4H^+ \longrightarrow 3Fe^{3+}+NO+2H_2O$$

$$Fe^{3+}+3OH^- \longrightarrow \underset{\text{(Brown)}}{Fe(OH)_3(s)}$$

$$Al^{3+}+3OH^- \longrightarrow \underset{\text{(White gelatinous)}}{Al(OH)_3(s)}$$

**Note**. Ammonium chloride controls the ionization of ammonium hydroxide (common ion effect). In the absence of ammonium chloride cations of subsequent groups such as $Zn^{2+}$ and $Mn^{2+}$ may also be precipitated along with the hydroxides of $Fe^{3+}$ and $Al^{3+}$. Ammonium chloride reduces the concentration of $OH^-$ by common ion effect and buffer action and thus prevents the metals of subsequent groups from being precipitated as hydroxides, which have of higher solubility product values than those of the hydroxides of group III cations.

---

*The presence of $Fe^{2+}$ or $Fe^{3+}$ ions can be tested before adding nitric acid. For this take 1 ml of original solution and add a few drops of potassium ferricyanide. Appearance of a deep blue colour or ppt. shows the presence of $Fe^{2+}$. Similarly take 1 ml of the group solution and add a few drops of potassium ferrocyanide. Appearance of a deep blue colour confirms the presence of $Fe^{3+}$.

**Table 8.13. Analysis of group III cations ($Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$)**

| | *Experiment* | *Observation* | *Inference* |
|---|---|---|---|
| 1. | Treat the brown ppt. of $Fe(OH)_3$ with dilute HCl and heat. | A yellow solution is obtained due to the formation of $FeCl_3$ | $Fe^{3+}$ indicated |
| | Divide the solution into two parts : | | |
| | (*i*) To one part add potassium ferrocyanide solution. | Deep blue colour or ppt. is obtained | $Fe^{3+}$ confirmed |
| | (*ii*) To the 2nd part of the solution add potassium sulphocyanide solution. | A deep red colouration results | $Fe^{3+}$ confirmed |
| 2, | (*i*) To the O.S. add a few drops of dilute HCl followed by potassium ferricyanide solution. | Deep blue colour or ppt. is obtained | $Fe^{2+}$ present |
| | (*ii*) To the O.S. add a few drops of HCl followed by potassium thiocyanate solution. | No colouration results | $Fe^{2+}$ present |
| 3. | Dissolve the white gelatinous ppt. in a minimum quantity of dil. HCl. Now add a few drops of blue litmus solution followed by ammonia solution until the solution becomes ammoniacal. | A blue floating ppt. in colourless solution (lake) | $Al^{3+}$ confirmed |

The chemistry underlying the tests (Table 8.13) performed to identify $Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$ ions is outlined below :

**Reactions**

1. The brown ppt. of $Fe(OH)_3$ dissolves in hot dilute HCl forming a yellow solution of ferric chloride

$$Fe(OH)_3 + 3HCl \longrightarrow \underset{\text{(Yellow)}}{FeCl_3(aq)} + 3H_2O$$

(*i*) Solution containing ferric (III) ions reacts with potassium ferrocyanide, $K_4[Fe(CN)_6]$ to give deep blue ppt. (Prussian blue).

$$Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{(Prussian blue)}\\ \text{Potassium ferri-}\\ \text{ferrocyanide}}}{KFe[Fe(CN)_6](s)} + 3K^+$$

(*ii*) Solution containing Fe (III) ions reacts with potassium thiocyanate solution to give a deep red colouration caused by ferri-thiocyanate ion, $[Fe(SCN)]^{2+}$.

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{(Deep red)}}{[Fe(SCN)]^{2+}(aq)}$$

2. (*i*) Solution containing $Fe^{2+}$ ions reacts with potassium ferricyanide to give deep blue ppt. (Turnbull's blue)

$$Fe^{2+} + K_3[Fe(CN)_6] \longrightarrow \underset{\substack{\text{(Turnbull's blue)} \\ \text{Potassium ferro-} \\ \text{ferricyanide}}}{KFe[Fe(CN)_6]} + 2K^+$$

(*ii*) Ferrous ions do not give any colouration with potassium thiocyanate solution.

3. A white gelatinous ppt. of $Al(OH)_3$ is obtained in the reaction solution which absorbs the blue colouring matter of litmus and turns blue.

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Al(OH)_3(s)$$

The ppt. of $Al(OH)_3$ absorbs blue colouring matter of litmus and floats in the body of the solution (lake test).

**Analysis of Group IV Cations ($Ni^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and $Co^{2+}$)**

In case the cations from group I, II and III are absent proceed for group IV.

Take 2-3 ml of the original solution and add to it 0·5 g $NH_4Cl$ and aqueous ammonia dropwise until it smells like ammonia, or take the solution of group III (when group III is absent) smell it and make it ammoniacal if necessary. Now pass $H_2S$ gas through a test portion. If a ppt. is formed, it shows the presence of group IV. Now pass $H_2S$ through the whole solution for sufficient time to ensure complete precipitation. If a precipitate (black, dirty white, or buff coloured) appears, group IV is present. Filter and separate the ppt. and reject the filtrate. Analyze the ppt. for group IV cations as given in the Table 8.14.

$$Zn^{2+} + H_2S \longrightarrow \underset{\text{(White)}}{ZnS(s)} + 2H^+$$

$$Ni^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{NiS(s)} + 2H^+$$

$$Mn^{2+} + H_2S \longrightarrow \underset{\text{(Buff)}}{MnS(s)} + 2H^+$$

$$Co^{2+} + H_2S \longrightarrow \underset{\text{(Black)}}{CoS(s)} + 2H^+$$

**Table 8.14. Analysis of group IV cations**
**($Ni^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and $Co^{2+}$)**

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| **Black ppt.** | | |
| 1. Dissolve the black ppt. by heating with a minimum volume of aqua-regia (3 parts HCl and 1 part $HNO_3$). Evaporate nearly to dryness. | Residue is obtained due to the formation of anhydrous chlorides of $Ni^{2+}$ or $Co^{2+}$ | $Ni^{2+}$ or $Co^{2+}$ present |
| Cool and dissolve in water. Divide the solution in three parts. | | |
| (*i*) To one part of the solution (or O.S.) add a few drops of dimethyl glyoxime followed by aqueous ammonia solution. | A bright red ppt. of bis (dimethylglyoximato) nickel (II) is obtained | $Ni^{2+}$ confirmed |
| (*ii*) The 2nd part of the solution (or O.S.) add acetic acid and a little $KNO_2$. Allow it to stand with occasional scratching and shaking. | A yellow ppt. of potassium cobaltinitrite is obtained | $Co^{2+}$ present |
| (*iii*) To the 3rd part of the solution (or O.S.) add 1 g of ammonium thiocyanate, 2 ml of amyl alcohol (or 2 ml acetone). Shake the contents well. | Blue colour in the organic solvent layer | $Co^{2+}$ confirmed |
| (*iv*) Both $Co^{2+}$ and $Ni^{2+}$ can also be confirmed by borax-bead test. | | |
| **Dirty white ppt.** | | |
| 2. Treat the dirty white ppt. with a small volume of dil. HCl. Boil the contents to remove $H_2S$. Cool the solution. | | |
| Divide the solution in two fractions. | | |
| (*i*) To one fraction of the solution add NaOH solution slowly. | A white ppt. appears which dissolves in excess of NaOH | $Zn^{2+}$ present |
| (*ii*) To the 2nd fraction of the solution add 1 ml of $K_4[Fe(CN)_6]$ solution. | A bluish white ppt. appears | $Zn^{2+}$ confirmed |
| 3. Perform charcoal cavity cobalt nitrate test with the original salt or with the white ppt. | A green mass confirms $Zn^{2+}$ | $Zn^{2+}$ confirmed |

**Buff coloured ppt.**

| | | | |
|---|---|---|---|
| 4. | (*i*) Take a part of the buff coloured ppt. and add dil. HCl. Boil the contents to boil off $H_2S$ gas. Cool the solution and add NaOH solution slowly. Warm a little. | A white ppt. $[Mn(OH)_2]$ is formed which turns brown due to atmospheric oxidation | $Mn^{2+}$ present |
| | (*ii*) Dissolve the other part of the ppt. (or the salt itself) in conc. $HNO_3$. Add 1 g of lead peroxide and boil the contents. Allow it to stand. | The solution acquires pink colour due to the formation of per-manganic acid | $Mn^{2+}$ confirmed |
| | (*iii*) Perform borax bead test with a little of the residue and note the colour of the bead. | Violet bead in oxidizing flame | $Mn^{2+}$ confirmed |

The chemistry underlying the tests (Table 8.14) performed to identify $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ ions is outlined below :

**Reactions**

1. Black ppt. of nickel sulphide and cobalt sulphide dissolves in aqua regia.

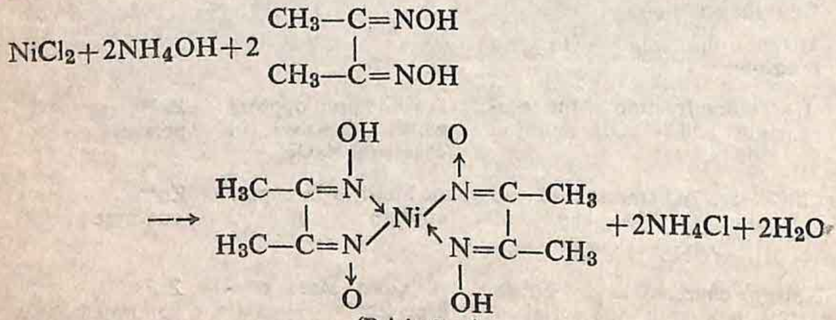
$$3NiS + 2HNO_3 + 6HCl \longrightarrow 3NiCl_2 + 2NO + 2S + 4H_2O$$

$$3CoS + 2HNO_3 + 6HCl \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

Hydrated chlorides on evaporation to dryness, yield residue of anydrous chlorides.

$$\underset{\text{(Green)}}{NiCl_2.6H_2O} \xrightarrow[\text{dryness}]{\text{Heat to}} \underset{\text{(Yellow)}}{NiCl_2} + 6H_2O$$

(*i*) A nickel salt solution reacts with dimethyl-glyoxime (DMG) solution in the presence of ammonia solution forming a bright red ppt. of bis (dimethyl-glyoximato) nickel (II) complex.



(Bright Red)

(*ii*) Cobalt salt solution reacts with $KNO_2$ solution in the presence of acetic acid forming a yellow crystalline ppt. of potassium cobaltinitrite.

$$Co^{2+}+7NO_2^{-}+3K^{+}+2H^{+} \longrightarrow K_3[Co(NO_2)_6]+NO+H_2O$$

(*iii*) With ammonium thiocyanate solution, cobalt ions form a blue coloured complex, ammonium cobalt thiocyanate, $NH_4[Co(CNS)_4]$.

This is a stable complex and gets extracted into organic solvent.

$$Co^{2+}+4NH_4CNS \longrightarrow \underset{\text{(Blue)}}{(NH_4)_2[Co(CNS)_4]}+2NH_4^{+}$$

2. White ppt. of zinc sulphide is soluble in dil. HCl. A colourless solution of zinc chloride is obtained and hydrogen sulphide escapes.

$$ZnS+2HCl \longrightarrow ZnCl_2(aq)+H_2S(g)$$

(*i*) Solution containing $Zn^{2+}$ ions on treating with sodium hydroxide solution gives a white ppt. of zinc hydroxide which dissolves in excess of alkali, forming soluble sodium zincate.

$$ZnCl_2+2NaOH \longrightarrow Zn(OH)_2(s)+NaCl$$

$$Zn(OH)_2+2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)}+2H_2O$$

(*ii*) Solution containing $Zn^{2+}$ reacts with potassium ferrocyanide solution and produces a bluish white ppt. of zinc hexacynoferrate (II).

$$2ZnCl_2+K_4[Fe(CN)_6] \longrightarrow 4KCl+\underset{\text{Zinc hexacyno-ferrate (II)}}{Zn_2[Fe(CN)_6]}$$

3. It has already been explained under the charcoal cavity test.

4. (*i*) Buff coloured ppt. of MnS is soluble in dil. HCl.

$$MnS+2HCl \longrightarrow MnCl_2+H_2S$$

Solution when treated with sodium hydroxide solution gives a white ppt. of manganese hydroxide which turns brown on exposure to atmospheric oxygen due to the formation of manganic hydroxide.

$$MnCl_2+2NaOH \longrightarrow \underset{\text{(White)}}{Mn(OH)_2(s)}+2NaCl$$

$$Mn(OH)_2+(O) \longrightarrow \underset{\text{Manganic hydroxide}}{MnO(OH)_2(s)}$$

(*ii*) The sulphide of manganese reacts with nitric acid to form manganese nitrate which in turn is oxidized by boiling with $HNO_3$ and $PbO_2$ to $MnO_4^{2-}$ ion, characterized by its pink colour.

$$MnS+2HNO_3 \longrightarrow Mn(NO_3)_2+H_2S$$

$$2Mn(NO_3)_2+5PbO_2+6HNO_3 \longrightarrow \underset{\substack{\text{Permanganic acid}\\ \text{(Pink)}}}{2HMnO_4(aq)}+5Pb(NO_3)_2+2H_2O$$

(*iii*) The chemistry of borax bead test has already been explained in the beginning of this unit.

**Analysis of Group V Cations ($Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$)**

When the first four groups are absent, take the original solution or take the solution of the fourth group. Add conc $(NH_4)_2CO_3$ solution with constant stirring to the above solution. Warm and allow to stand. Formation of a white ppt. indicates the presence of group V. Filter the ppt. Analyze the ppt. for the group V cations as given in the Table 8.14 and reject the filtrate.

$$Ca^{2+}+CO_3^{2-} \longrightarrow CaCO_3(s)$$
$$Ba^{2+}+CO_3^{2-} \longrightarrow BaCO_3(s)$$
$$Sr^{2+}+CO_3^{2-} \longrightarrow SrCO_3(s)$$

**Table 8.15. Analysis of group V cations ($Ba^{2+}$, $Sr^{2+}$ and $Ca^{2+}$)**

The white ppt. may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$. Wash the ppt. with hot water and reject washings. Dissolve the ppt. in minimum amount of hot dil. $CH_3COOH$. Divide the solution in four parts.

$$BaCO_3+2CH_3COOH \longrightarrow Ba(CH_3COO)_2+H_2O+CO_2$$
$$CaCO_3+2CH_3COOH \longrightarrow Ca(CH_3COO)_2+H_2O+CO_2$$
$$SrCO_3+2CH_3COOH \longrightarrow Sr(CH_3COO)_2+H_2O+CO_2$$

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| 1. To one part of the solution add potassium chromate solution. | A yellow ppt. of barium chromate is obtained. | $Ba^{2+}$ confirmed |
| 2. To the 2nd part of the solution add dil. $H_2SO_4$ solution. | A white ppt. of $BaSO_4$ is obtained. The ppt. is insoluble in all mineral acids. | $Ba^{2+}$ confirmed |
| 3. Perform flame test with the salt or with the ppt. obtained in test 1. (Group ppt. *i.e.*, carbonate can also be used for the flame test). | A light green flame. | $Ba^{2+}$ confirmed |
| 4. To the 3rd part of the solution add conc. solution of $(NH_4)_2SO_4$ and warm if necessary. | A white ppt. of $SrSO_4$ is obtained. | $Sr^{2+}$ confirmed |
| 5. Perform the flame test with the salt. | A crimson colour flame. | $Sr^{2+}$ confirmed |
| 6. (*i*) To the 4th part of the solution add conc. ammonium oxalate solution and heat. | A white ppt. of calcium oxalate is obtained. | $Ca^{2+}$ confirmed |
| (*ii*) Add to the ppt. obtained, dil. $H_2SO_4$ or HCl. Now add a few drops of dilute $KMnO_4$ solution. | Pink colour of $KMnO_4$ solution is discharged. | $Ca^{2+}$ confirmed |
| 7. Perform flame test with the salt or with the ppt. obtained in test 6. | A brick red flame is seen. | $Ca^{2+}$ confirmed |

The chemistry underlying the tests (Table 8.15) performed for identifying the group V cations is outlined below :

**Reactions**

1. Solution of barium acetate reacts with potassium chromate to form a yellow ppt. of barium chromate.

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\text{(Yellow)}}{BaCrO_4(s)} + 2CH_3COOK$$

2. Solution of barium acetate reacts with dilute $H_2SO_4$ to yield a white crystalline ppt. of barium sulphate which is insoluble in all acids.

$$(CH_3COO)_2Ba + H_2SO_4 \longrightarrow \underset{\text{(White)}}{BaSO_4(s)} + 2CH_3COOH$$

3. The principle of flame test has already been explained.

4. Solution of strontium acetate reacts with ammonium sulphate solution forming a white ppt. of strontium sulphate which is insoluble in mineral acids.

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow \underset{\text{(White)}}{SrSO_4(s)} + 2CH_3COONH_4$$

5. The principle of the flame test has already been explained.

6. (*i*) Solution of calcium acetate reacts with ammonium oxalate to yield a white ppt. of calcium oxalate.

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{(White)}}{CaC_2O_4(s)} + 2CH_3COONH_4$$

(*ii*) The ppt. of calcium oxalate is soluble in dil. HCl or $H_2SO_4$ and forms the corresponding salt solution.

$$CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4 \text{ [or } (COOH)_2]$$

The solution acts as a reducing agent due to the presence of oxalate ions and discharges the colour of $KMnO_4$ solution.

**Analysis of Group VI Cations ($Na^+$, $K^+$, $Mg^{2+}$, and $NH_4^+$)**

This group includes those elements which are not precipitated by other group precipitating reagents. There is, however, no group test for these cations and the different cations are tested individually as given in Table 8.16. ($Mg^{2+}$, $Na^+$ and $K^+$ may be tested from the solution of the group V also, but the process being tedious is not described here).

### Table 8.16. Analysis of group VI cations ($Na^+$, $K^+$ $Mg^{2+}$ and $NH_4^+$)

| *Experiment* | *Observation* | *Inference* |
|---|---|---|
| 1. To the O.S. of the salt add solid $NH_4Cl$ followed by disodium hydrogen phosphate solution (or ammonium phosphate. Mix the contents thoroughly. Add an aqueous solution of ammonia until it smells of ammonia. Add a few ml of ethanol and scratch the sides of the test tube with a glass rod. | A fine crystaline white ppt. appears on scratching the sides of the test tube. | $Mg^{2+}$ confirmed |
| 2. (*i*) Heat the given salt with a few ml of sodium hydroxide solution. | Ammonia gas evolves. | $NH_4^+$ present |
| (*ii*) Bring a glass rod dipped into hydrochloric acid near the exit of gas. | Dense white fumes of ammonium chloride are obtained. | $NH_4^+$ confirmed |
| 3. To the O.S., add a few drops of NaOH to make it alkaline. Now add 1-2 ml of Nessler's reagent solution. | A brown ppt. (iodide of Millon's base) is obtained. | $NH_4^+$ confirmed |
| 4. To 1-2 ml of the O.S. of the salt add a few drops of acetic acid and freshly prepared solution of sodium cobaltinitrite. Shake and allow it to stand. | A bright yellow ppt. of $K_2Na[Co(NO)_6]$ is obtained. | $K^+$ present |
| 5. Perform the flame test with the original solid. | A violet flame but intense violet red (or crimson) through blue glass. | $K^+$ confirmed |
| 6. To 1-2 ml of the salt solution add a small volume of potassium dihydro antimonate solution. Warm the solution and scratch the inside of the test tube with a glass rod. | A crystalline white ppt. of $NaH_2SbO_4$ which sticks to the wall of the test tube. | $Na^+$ present |
| 7. Perform the flame test with the original salt. | A golden yellow flame but invisible through blue glass. | $Na^+$ confirmed |

**Note :** While performing the tests of $K^+$ and $Na^+$ ammonium salts should be absent as they tend to interfere in their detection.

The chemistry involved in the tests (Table 8.16) performed for identifying $Na^+$, $K^+$ and $NH_4^+$ ions is given on next page.

**Reactions**

1. A magnesium salt solution reacts with a phosphate in the presence of ammonia to form a fine crystalline white ppt. of magnesium ammonium phosphate hexahydrate.

$$Mg^{2+} + HPO_4^{2-} + NH_4OH + 5H_2O \longrightarrow \underset{\text{(White ppt.)}}{MgNH_4PO_4.6H_2O}$$

Ethanol decreases the solubility of ppt.

2. (*i*) Ammonium salt on heating with sodium hydroxide gives ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NaCl + H_2O + \underset{\text{Ammonia}}{NH_3(g)}$$

(*ii*) Ammonia gas reacts with the vapours of HCl forming dense white fumes of ammonium chloride.

$$NH_3 + HCl \longrightarrow \underset{\text{(Dense white fumes)}}{NH_4Cl(s)}$$

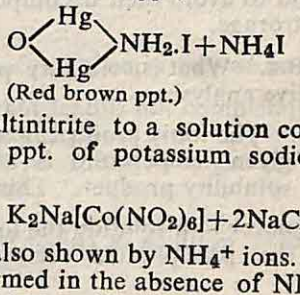
3. Alkaline solution of ammonium salt reacts with Nessler's reagent. A red brown ppt. of the iodide of Millon's base, $NH_2Hg_2I_3$ is obtained.

$$NH_4^+ + NaOH \longrightarrow NH_3 + H_2O + Na^+$$

$$\underset{\text{Nessler's reagent}}{K_2HgI_4} \longrightarrow 2KI + HgI_2$$

$$HgI_2 + 2NH_3 \longrightarrow Hg(NH_2)I + NH_4I$$

$$Hg(NH_2)I + HgI_2 \longrightarrow \underset{\text{(Red brown ppt.)}}{NH_2Hg_2I_3(s)} \quad \text{or} \quad [Hg_2I_2NH_2]I$$



$$\text{or} \quad 2(H_2N-Hg-I) + H_2O \longrightarrow \underset{\text{(Red brown ppt.)}}{O\langle^{Hg}_{Hg}\rangle NH_2.I} + NH_4I$$

4. Addition of sodium cobaltinitrite to a solution containing $K^+$ ions gives a yellow crystalline ppt. of potassium sodiocobaltinitrite.

$$2KCl + Na_3[Co(NO_2)_6] \longrightarrow K_2Na[Co(NO_2)_6] + 2NaCl$$

The precipitation reaction is also shown by $NH_4^+$ ions. Hence the test for $K^+$ ion should be performed in the absence of $NH_4^+$ ion. If $NH_4^+$ ions are present they should be removed from the solution by boiling it with $Na_2CO_3$ or NaOH before performing the test.

5. The chemistry of the flame test has already been discussed in the beginning of this unit.

6. Weakly alkaline or neutral solution of sodium compounds when treated with a solution of potassium dihydroantimonate gives a white crystalline ppt. of sodium dihydroantimonate.

$$NaCl + KH_2SbO_4 \longrightarrow \underset{\text{(White)}}{NaH_2SbO_4(s)} + KCl$$

7. The chemistry of the flame test has already been discussed.

## ORAL QUESTIONS AND ANSWERS

**Q. 8.1.** Why is it necessary to prepare original solution for the detection of basic radicals ?

**Ans.** The detection of basic radicals depends on the behaviour of ions in solution. For this purpose the preparation of original solution is necessary as it furnishes free ions in solution.

**Q. 8.2.** Why do we not prefer to prepare original solution in conc. $H_2SO_4$ or conc. $HNO_3$ ?

**Ans.** It is not advisable to prepare original solution in conc. $HNO_3$ or conc. $H_2SO_4$ because these are oxidizing agents and they oxidize $H_2S$ in group II to produce a yellow ppt. of sulphur.

$$H_2SO_4 \longrightarrow H_2O+SO_2+[O]$$

$$HNO_3 \longrightarrow H_2O+NO_2+[O]$$

$$H_2S+O \longrightarrow H_2O+\underset{\text{(Yellow)}}{S(s)}$$

Also Pb, Ba, Sr, Ca are precipitated as their insoluble sulphates in presence of conc. $H_2SO_4$.

$$BaCl_2+H_2SO_4 \longrightarrow \underset{\text{(Insoluble)}}{BaSO_4(s)}+2HCl$$

**Q. 8.3.** Why are hydrogen peroxide and silver nitrate kept in coloured bottles ?

**Ans.** Hydrogen peroxide and silver nitrate are decomposed by sunlight and to avoid their decomposition coloured bottles are used for their strorage.

**Q. 8.4.** What is solubility product ? Explain its importance in qualitative analysis.

**Ans.** The ionic product in a saturated solution of an electrolyte at a given temperature is always a constant quantity and is termed as solubility product. This is denoted by symbol S.

Whenever in a solution the ionic product exceeds the solubility product, the precipitation occurs due to the supersaturation of solution.

**Q. 8.5.** Why do salts of the following ions $Cu^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$, $Na^{2+}$ and $K^+$ impart colour to the flame ?

**Ans.** This is due to the fact that the chlorides of these cations are volatile and at higher temperature they ionize giving respective cations. These cations then impart colour to the flame.

**Q. 8.6.** Why is platinum wire used for flame test ?

**Ans.** This is because the metals other than platinum are attacked by conc. HCl, while platinum wire does not react with conc. HCl even at very high temperature.

**Q. 8.7.** Can we perform the charcoal cavity test without the addition of fusion mixture ($Na_2CO_3$ and $K_2CO_3$) with the carbonate of metals ?

**Ans.** Yes, we can directly perform the charcoal cavity test without the addition of fusion mixture because the latter simply converts the substances into carbonates in fused state. Carbonates of metals on heating in charcoal cavity are reduced to metallic state.

**Q. 8.8.** Why do we not perform borax bead test with the white salts ?

**Ans.** This test is applied for the identification of the cations of the coloured salt only because the borax forms the corresponding metaborates which possess characteristic colour. For example, with $CuSO_4$, the reaction is

$$\underset{}{CuSO_4}+\underset{\text{(From borax)}}{B_2O_3} \longrightarrow \underset{\text{(Blue)}}{Cu(BO_2)_2}+SO_3$$

**Q. 8.9.** Why are only $Pb^{2+}$, $Ag^+$ and $Hg_2^{2+}$ ions precipitated in group I ?

**Ans.** Out of all the chlorides, those of $Pb^{2+}$, $Ag^+$ and $Hg_2^{2+}$ are insoluble. HCl is the reagent of group I. Thus, chlorides of $Pb^{2+}$, $Ag^+$, and $Hg_2^{2+}$ are precipitated in group I.

$$AgNO_3+HCl \longrightarrow \underset{\text{(White ppt.)}}{AgCl(s)}+HNO_3$$

Other cations remain in solution because their chlorides are soluble.

**Q. 8.10.** Why is lead placed in group I as well as in II ?

**Ans.** This is due to fact that lead is not completely precipitated in group I as lead chloride. $PbCl_2$ is also soluble in hot water. Therefore, the lead which escapes precipitation in group I as $PbCl_2$ is precipitated in the group II as PbS.

**Q. 8.11.** Is it necessary to acidify a solution before group II cations are precipitated with $H_2S$ ?

**Ans.** Yes, because for the precipitation of cations of group II only small concentration of sulphide ions ($S^{2-}$) is required.

This condition is achieved by passing $H_2S$ gas in a solution acidified with HCl (dil.). Due to common ion effect, concentration of $S^{2-}$ ions decreases as presence of hydrochloric acid suppresses the ionization of $H_2S$—resulting only in the precipitation of sulphides of group II metals.

Other metal sulphides remain in solution as they require higher concentration of $S^{2-}$ ions for their precipitation.

**Q. 8.12.** Give the reason for the formation of a light yellow or white ppt. in the group II even if it may not be because of some metal ion.

**Ans.** Yellow or white ppt. is formed due to the oxidation of $H_2S$ gas by some oxidizing agents to sulphur which floats on the surface.

$$BaSO_3+2HCl+2H_2S \longrightarrow BaCl_2+3H_2O+\underset{\text{(Yellow)}}{3S}$$

$$2NaNO_3+H_2S+2HCl \longrightarrow 2NO+2NaCl+2H_2O+\underset{\text{(Yellow)}}{S}$$

$$FeCl_3+H_2S \longrightarrow 2FeCl_2+2HCl+\underset{\text{(Yellow)}}{S}$$

**Q. 8.13.** What is the use of adding nitric acid in the precipitation of group II cations as hydroxides.

**Ans.** Nitric acid is useful in the oxidation of ferrous salts to ferric salts in group III.

$$2FeSO_4+4HNO_3 \longrightarrow Fe_2(SO_4)_3+Fe(NO_3)_3+2NO+2H_2O$$

**Q. 8.14.** Why is it essential to oxidize ferrous salt to ferric salt ?

**Ans.** This is because the ferrous salts are not completely precipitated as $Fe(OH)_2$ in the presence of $NH_4Cl$ on the addition of $NH_4OH$ and thus iron will also be precipitated in the group IV as FeS on passing $H_2S$.

Therefore, to precipitate iron completely in the group III, it is necessary to oxidize ferrous salt to ferric salt.

**Q. 8.15.** Why do we add excess of $NH_4OH$ and $NH_4Cl$ in the precipitation of group III cations ?

**Ans.** The solubility product of hydroxides of cations of group III is extremely low.

$NH_4Cl$ suppresses the ionization of $NH_4OH$ to a great extent due to common ion effect. As a result, low concentration of $OH^-$ is made available for precipitating group III cations hydroxides.

Other hydroxides remain in solution as they require higher concentration of $OH^-$ ions for precipitation as hydroxides.

**Q. 8.16.** Can $NH_4Cl$ be replaced by any other ammonium salt for the precipitation of group III cations ?

**Ans.** Yes, $NH_4NO_3$ can be used in place of $NH_4Cl$ for the precipitation of group III cations. Ammonium sulphate cannot be used as it may precipitate $Ca^{2+}$, $Ba^{2+}$, and $Sr^{2+}$ as insoluble sulphates.

**Q. 8.17.** Why are Zn, Mn, Ni, Co not precipitated in the group III as hydroxides ?

**Ans.** The solubility product of hydroxides of Zn, Mn, Ni and Co is very high. For this purpose they require high concentration of

$OH^-$ ions. This is not possible in the group III as $NH_4Cl$ suppresses the ionization of $NH_4OH$ due to common ion effect.

**Q. 8.18.** Why are the group IV cations not precipitated as sulphides on passing $H_2S$ gas through group II solution ?

**Ans.** For the precipitation of cations of group IV, a very large concentration of sulphide ions ($S^{2-}$) is required which is not available in the group II as the ionization of $H_2S$ is suppressed by HCl (common ion effect).

In precipitating the cations of group IV, high concentration of $S^{2-}$ ions is reached as $OH^-$ ions released by $NH_4OH$ unite with $H^+$ ions given by $H_2S$. Thus the solubility product is exceeded and the cations of group IV are precipitated as ZnS, NiS, MnS and CoS.

**Q. 8.19.** Why is, at times, a black coloured precipitate obtained in group IV even if nickel and cobalt ions are not present ?

**Ans.** A black coloured precipitate is obtained in the group IV due to the incomplete removal of iron in group III. Iron escapes precipitation in group III due to lack of enough $NH_4OH$.

$$FeCl_2 + H_2S \longrightarrow \underset{\text{(Black ppt.)}}{FeS(s)} + 2HCl$$

**Q. 8.20.** Can $Na_2CO_3$ be used as a precipitating agent for group V cations in place of $(NH_4)_2CO_3$ ?

**Ans.** Sodium carbonate cannot be used as a precipitating agent for group V cations due to its highly ionizing nature which may also precipitate magnesium in group V.

**Q. 8.21.** Why is carbonate (precipitate) of group V cations dissolved in acetic acid ?

**Ans.** This is because the acetic acid is a weak acid and does not interfere in the test.

If dil. $H_2SO_4$ is used for this purpose, it will precipitate sulphates of Ca, Ba and Sr.

In the presence of dil. HCl or $HNO_3$, calcium will not give a precipitate with ammonium oxalate as the acids will dissolve the ppt. calcium oxalate.

**Q. 8.22.** Why do we analyze group V cations strictly in the order of Ba, Sr and Ca ?

**Ans** This is because only chromate of barium is insoluble in acetic acid. Both sulphate and oxalate of Ba are also insoluble in acetic acid.

Chromates of both Sr and Ca are soluble in acetic acid. Both sulphate and oxalate of Sr are insoluble.

**Q. 8 23.** Why is a precipitate of magnesium carbonate not formed along with the carbonates of Ba, Sr and Ca in group V ?

**Ans.** Magnesium requires higher concentration of $CO_3^{2-}$ ions for its precipitation as $MgCO_3$ which is insufficient in group V due to the presence of $NH_4Cl$ along with $(NH_4)_2CO_3$.

$NH_4Cl$ suppresses the ionization of $(NH_4)_2CO_3$ thereby a low concentration of $CO_3^{2-}$ ions is made available due to common ion effect.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$(NH_4)_2CO_3 \rightleftharpoons \underset{\text{(Common ion)}}{2NH_4^+} + \underset{\text{(Low concentration)}}{CO_3^{2-}}$$

**Q. 8.24.** Why is a freshly prepared solution of $FeSO_4$ used for the detection of nitrate and nitrite ?

**Ans.** This is because $Fe^{2+}$ ions on long standing are oxidized to $Fe^{3+}$ ions which is not used for the detection of nitrate or nitrite.

**Q. 8.25.** How will you distinguish between ferrous and ferric salts ?

**Ans.** Ammonium sulphocyanide does not give any colouration with ferrous salt while it gives a blood red colour with ferric salt.

Potassium ferricyanide produces a blue ppt. with ferrous salt while a red colouration is obtained with ferric salt.

**Q. 8 26** Can we replace $BaCl_2$ by $Ba(NO_3)_2$ in the detection of $SO_4^{2-}$ ion ?

**Ans.** We can use $Ba(NO_3)_2$ in place of $BaCl_2$ for the detection of $SO_4^{2-}$ ion as we require only $Ba^{2+}$ ion for the precipitation of sulphate as $BaSO_4$.

$$ZnSO_4 + BaCl_2 \longrightarrow BaSO_4\,(s) + ZnCl_2$$

$$ZnSO_4 + Ba(NO_3)_2 \longrightarrow BaSO_4\,(s) + Zn(NO_3)_2$$

**Q. 8.27.** How will you distinguish between carbonate and bicarbonate ions ?

**Ans.** $MgSO_4$ gives a white ppt. with carbonate ions in cold solution while a white ppt. is obtained with bicarbonate ions in hot solution only.

Phenolphthalein gives a pink colour with carbonate ions and no colour is obtained with bicarbonate ions.

**Q. 8.28.** How can sulphide ions be distinguished from sulphite ions ?

**Ans.** $AgNO_3$ forms white ppt. with sulphite ions while a black precipitate is obtained with sulphide ions.

$BaCl_2$ gives white ppt. with sulphite ions while no ppt. is obtained with sulphide ions.

$FeCl_3$ solution gives a red colouration with sulphite ions and a black ppt. is formed with sulphide ions.

**Q. 8.29.** How will you distinguish between sulphate and thiosulphate ions ?

**Ans.** $AgNO_3$ gives white ppt. with thiosulphate ions which turns black on standing whereas no ppt. is obtained with sulphate ions.

$FeCl_3$ gives purple colour, with thiosulphate which disappears gradually and no ppt. or colouration is obtained in case of sulphate.

**Q. 8.30.** How will you distinguish between sulphite and sulphate ions ?

**Ans.** $BaCl_2$ gives a white ppt. with both sulphite and sulphate ions.

$BaSO_3$ is soluble in conc. HCl whereas $BaSO_4$ is insoluble in conc. HCl.

$FeCl_3$ solution gives a red colour with sulphite and no colour is obtained with sulphate.

**Q. 8.31.** How can nitrite ion be distinguished from nitrate ion ?

**Ans.** Nitrate ion gives a brown ring with $FeSO_4$ and conc. sulphuric acid. But with nitrite ion a black coloured solution is obtained.

**Q. 8.32.** Why does a paper soaked in $K_2Cr_2O_7$ solution turn green in the detection of $SO_3^{2-}$ ion ?

**Ans.** The paper turns green because the $SO_2$ gas evolved from $SO_3^{2-}$ salt reduces $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$ which turns the paper green.

**Q. 8.33.** What is lime water ?

**Ans.** It is a water solution of calcium hydroxide.

**Q. 8.34.** Is it necessary to treat a salt with HCl before performing a flame test ?

**Ans.** Yes, hydrochloric acid is used to convert a salt into its chloride. Metal chlorides being volatile, respond to the test.

**Q. 8.35.** Why do we prefer HCl for preparing solutions of cations ?

**Ans.** Because most of the salts are soluble in HCl except those of group I.

**Q. 8.36.** Why is it essential to boil off $H_2S$ gas before proceeding to group III ?

**Ans.** Otherwise the sulphides of group IV will also be precipitated along with precipitate of group III.

□ □

# UNIT 9

# Volumertic (Titrimetric) Analysis

## 9.1. Introduction

Volumetric (Titrimetric) analysis is the quantitative determination of the components of a mixture. The measured volumes of two solutions are made to react so that the reation is just complete. In volumetric analysis, one solution of known concentration is used. This is termed as the **volumetric standard**. One of the two solutions is put in a measuring vessel known as a burette. This could be a standard solution ; it is then gradually added to the solution to be analyzed until the reaction is complete. This operation is known as titration. The progress of a reaction is followed by an indicator ; the indicator is used to determine the completion of a reaction (stoichiometric point) usually by a colour change. The correctness of volumetric results depends upon the measuring vessels, measurement of volumes and weighing.

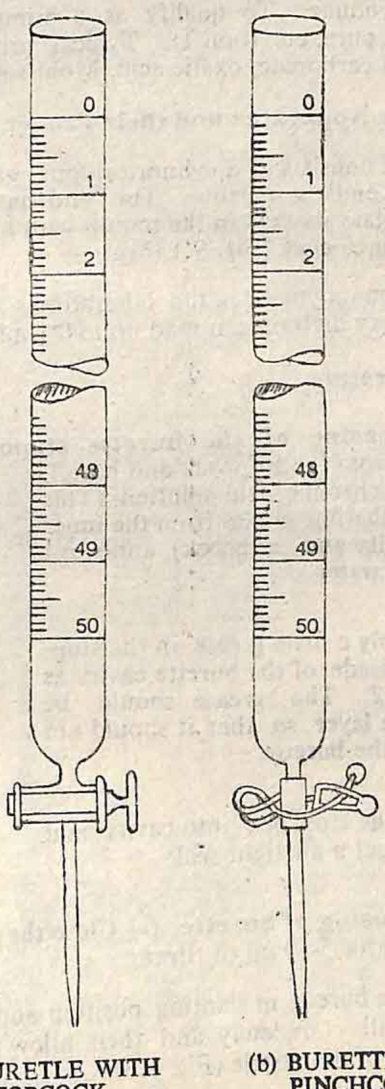
Volumetric analysis has certain advantages over the other methods of quantitative analysis, such as gravimetric analysis. These are :

1. Volumetric analysis does not involve laborious and tedious operations, such as precipitation, filtration, washing, drying and ignition.

2. Volumetric determinations are more rapid and accurate.

## 9.2. Requirements for Reactions used in Volumetric Analysis

A common practice in volumetric analysis is to make a standard solution of one reagent and use it to find the concentration of the other. To the measured volume of one solution is added another solution until the reaction is complete. The point in a titration when the amount of titrant added is the stoichiometric amount needed to react with the measured amount of the other reagent is called the **equivalence point**. It is, therefore, obivious that it is necessary in titration to determine the equivalence point with sufficient accuracy. It is on this point that calculation of results is based. In order to recognize the equivalence point it is necessary to monitor the progress of titrations. It is customary to use certain substances called indicators (substances which change colour when the pH of their solution alter) which usually show a marked colour change at the completion of the reaction. The point at which the colour change of the indicator becomes apparent to the eye is called the **end point**. Thus the end point of titration is the point at which the indicator shows the reaction to be complete. At times, there is a difference between the stoichiometric and practical end point This difference is termed as titration error. The choice of indicator



(a) BURETLE WITH STOPCOCK (b) BURETTE WITH PINCHCOCK

Fig. 9.1. Variety of burettes.

should be such that the titration error is as small as possible by controlling the experimental conditions.

It is essential in a titration that at least one solution is of exactly known concentration (volumetric standard). Its concentration may be determined from another titration, but there must be a substance in the analytical procedure which is a primary standard. A primary standard is a substance which can be converted into a standard solution by weighing the material out accurately on an analytical balance and dissolving it in water to obtain a solution of exactly known volume. To qualify as a primary standard, the substance must be pure, etc. (unit I). Typical primary standard are anhydrons sodium carbonate, oxalic acid, Mohr's salt, etc.

## 9.3. Volumetric Apparatus and their Proper Use

**Burette**. It consists of a cylindrical long glass tube graduated in ml. One of its ends is narrow. This end has either a glass tap [Fig. 9.1(*a*)] or a glass jet held in the mouth with a rubber tubing and operated with a pinch-cock [Fig. 9.1 (*b*)].

Burettes commonly used in the laboratories are graduated from 0 to 50 ml and every division can read up to 0·1 ml.

**How to use a burette :**

**Step I. Greasing of the burette stopcock.** (*i*) Remove all the old grease from the stopcock and barrel. Then clean it with chromic acid solution. (This will remove any adhering grease from the inner surface of the cavity and stopcock) and wash it thoroughly with water.

(*ii*) Now apply a little grease on the stopcock and the inner side of the burette cavity as shown in Fig. 9.2. The grease should be applied in a thin layer so that it should not choke the hole of the burette.

(*iii*) Insert the stopcock into cavity and rotate it gently to get a air tight seal.

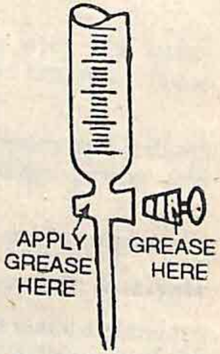


Fig. 9.2. Greasing of burette

**Step II. Rinsing of burette.** (*i*) Close the stopcock, and fil the burette with about 5-10 ml of titrant.

(*ii*) Hold the burette in slanting position and rotate it twice or thrice to wet the walls completely and then allow the liquid to run out through the tip of the nozzle (Fig. 9.3).

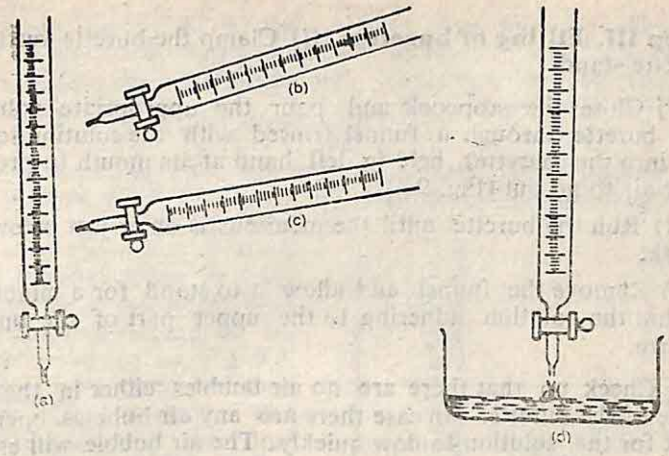


Fig. 9.3. Rinsing a burette

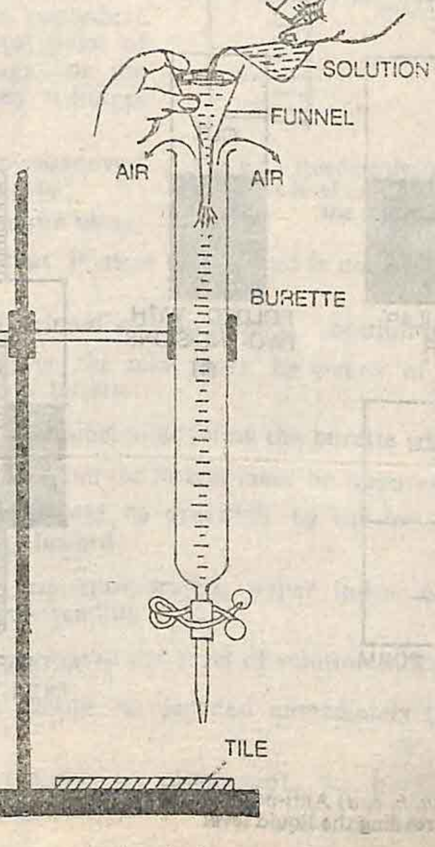


Fig. 9.4. Filling the burette with a titrant

**Step III. Filling of burette.** (*i*) Clamp the burette vertically in a burette stand.

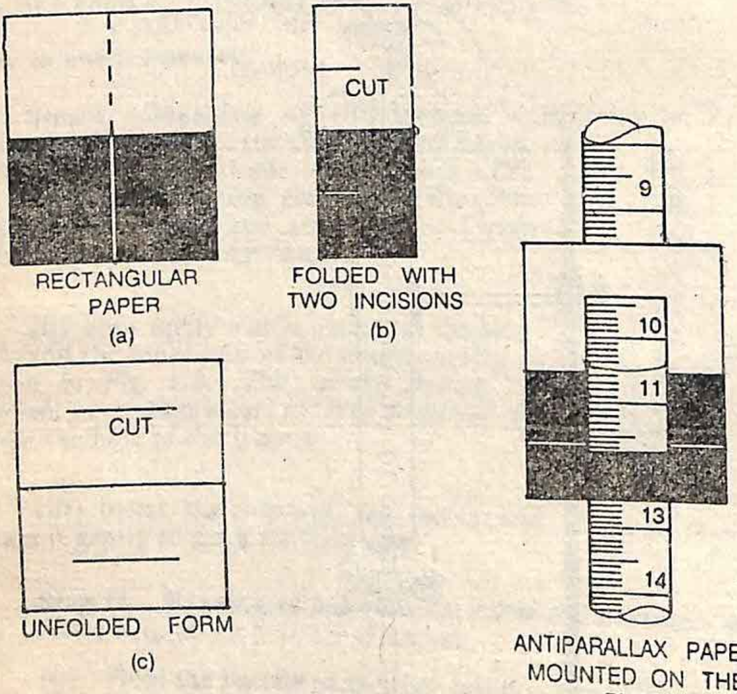
(*ii*) Close the stopcock and pour the appropriate solution into the burette through a funnel (rinsed with the solution to be poured into the burette), held in left hand at its mouth to provide space for air to go out (Fig. 9.4).

(*iii*) Run the burette until the meniscus is on or just below the zero mark.

(*iv*) Remove the funnel and allow it to stand for a minute or two so that the solution adhering to the upper part of the burette drips down.

(*v*) Check up that there are no air bubbles either in the tube or nozzle of the burette. In case there are any air bubbles, open the stopcock for the solution to flow quickly. The air bubble will escape quickly.

**Step IV. Taking the burette reading.** This involves the following steps :



RECTANGULAR PAPER (a)

FOLDED WITH TWO INCISIONS (b)

UNFOLDED FORM (c)

ANTIPARALLAX PAPER MOUNTED ON THE BURETTE (d)

Fig. 9.5. (*a, b, c, d*) **Anti-parallax paper index ; correct method of reading the liquid level** (*i*) **Removal of parallax.** It is done with the help of *anti-parallax paper index* and is prepared by folding a rectangular piece of white paper into two halves and then giving to it incisions at two places [Fig. 9.5 (*a* and *b*)]. Now open the fold and mount the paper index on the burette [Fig. 9 5 (*c*) and (*d*)].

(*ii*) **Reading the correct meniscus**. Anti-parallax paper index is allowed to slip over the burette and is finally held against the level of the solution. Keep your eye in level with the lower meniscus of the solution and the black boundary, and note the *initial reading* of the burette as shown in Fig. 9.6. Similarly note down the *final reading* of the burette. The difference between the final reading and the initial reading gives the volume of the solution used for titration.

The standard procedure is to read the lowest point of liquid when it sags or the highest point when it bulges upward.

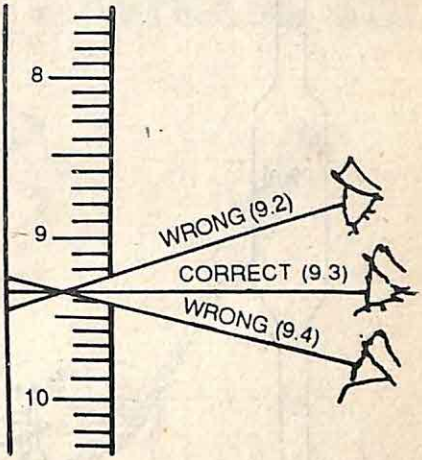


Fig. 9.6. Reading the correct meniscus at eye level *i.e.*, the correct level of the solution

**Precautions to be observed while using a burette**

(*i*) Clean it before using.

(*ii*) Ensure that it runs freely and is not blocked by dirt or grease.

(*iii*) It must be rinsed with appropriate solution before use.

(*iv*) Fill it above the zero mark by means of a funnel. It should not rest on the burette.

(*v*) Remove the funnel after filling the burette with titrant.

(*vi*) Air bubbles from the nozzle must be removed.

(*vii*) Stopcock should be operated by the left hand and the stopper kept pressed inward.

(*viii*) Always use anti-parallax paper index when taking a reading. It facilitates reading.

(*ix*) Adjust your eye at the level of solution in the burette.

(*x*) Reading should be recorded immediately in the practical record book.

(*xi*) Having finished the experiment, the burette should be thoroughly washed with water.

**Pipette.** It is another measuring vessel to measure the volume of solution to be delivered. Pipettes of known volume say 10 ml, 20 ml, 25 ml or 100 ml are available in the market and the selection of a pipette of suitable volume can be made at the time of titration. This measurement is correct at a temperature engraved on the bulb of the pipette. It consists of a narrow tube with a bulged out bulb in its middle. One of its ends is drawn out into a nozzle and the other one bears an etched circular mark (Fig. 9.7). This mark fixes a limit upto which the pipette should be filled to make a volume etched on the bulb.

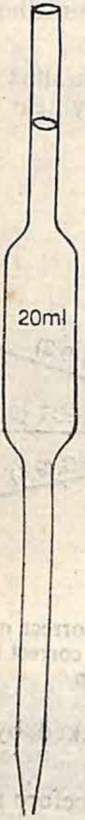


Fig. 9.7. A pipette

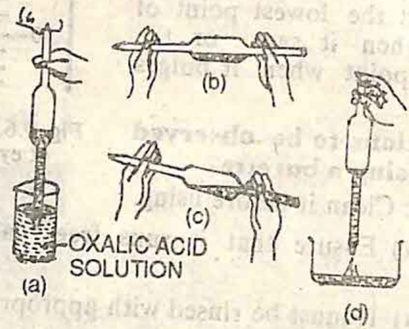


Fig. 9.8. Rinsing a pipette : (*a*) Suck the solution to be titrated into pipette, (*b*) Hold the pipette between two hands, (*c*) Tilt the pipette gradually and keep on rotating for some time, and (*d*) Run out the rinsed solution into the sink.

**How to use a pipette :**

(*i*) Clean the pipette with chromic acid solution and wash it thoroughly with water. Now rinse it with the solution to be measured. For rinsing, suck about 5 ml of the solution into it. Hold the pipette between two hands. Tilt and rotate it so that the inner walls of the pipette come in the contact of the solution. Allow the rinsed solution to run out into the sink (Fig. 9.9).

(*ii*) Now place the narrow tip of the pipette well below the surface of the liquid and suck the solution from the other end until the solution rises well above the circular edged mark. Now place your forefinger of the right hand at the mouth end firmly [Fig. 9.9 (*a*) and (*b*)].

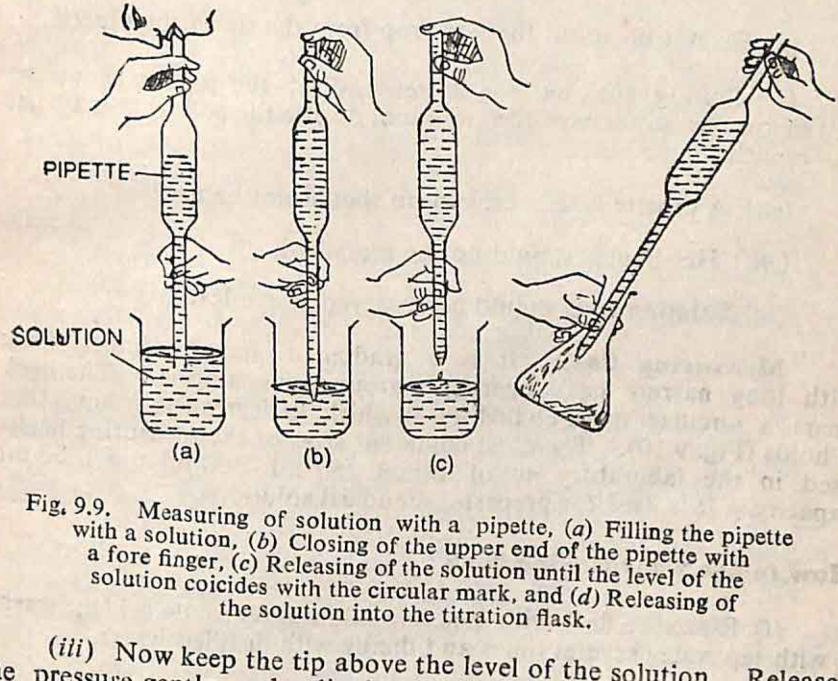


Fig. 9.9. Measuring of solution with a pipette, (*a*) Filling the pipette with a solution, (*b*) Closing of the upper end of the pipette with a fore finger, (*c*) Releasing of the solution until the level of the solution coicides with the circular mark, and (*d*) Releasing of the solution into the titration flask.

(*iii*) Now keep the tip above the level of the solution. Release the pressure gently so that liquid gradually moves downward. Continue to allow the level of the solution to fall slowly until the lower meniscus touches the etched mark when viewed by placing the eye at its level [Fig. 9.9 (*c*)].

(*iv*) Carefully move the pipette to the titration flask and introduce its tip into the titration flask [Fig. 9.9 (*d*)]. Now release the pressure completely by removing the forefinger. Wait for a few seconds for the solution to run out completely. Do not blow it out.

(*v*) Touch the tip of the pipette against the walls of the flask [Fig. 9.9 (*d*)] and hold it in the flask for 10 seconds. Remove the pipette.

(*vi*) Students will find a drop or two still left in the jet end of the pipette. This should not be blown out because it has already been accounted for while calibrating the pipette.

**Precautions to be observed while using a pipette :**

(*i*) Clean the pipette with chromic acid and finally wash it with distilled water.

(*ii*) Rinse the pipette properly with the solution to be delivered.

(*iii*) Never suck too fast lest the solution should rush into your mouth. Do not suck poisonous solutions into the pipette.

(*iv*) Forefinger used to hold the solution must be dry.

(*v*) Do not blow out the last drop from the tip of the pipette.

(*vi*) During sucking, the lower end of the pipette should be well below the surface of the solution, or else the solution may get into mouth.

(*vii*) A pipette with a broken tip should not be used.

(*viii*) Hot liquids should not be measured.

(*ix*) Solution level should be observed at eye-level.

**Measuring flask**. It is a graduated flat bottomed flask with long narrow neck bearing a ground glass stopper. The neck bears a circular mark etched on it which indicates the volume that it holds (Fig. 9.10). The most common sizes of the measuring flasks used in the laboratory are of 100 ml, 250 ml, 500 ml and 1000 ml capacity. It is used for preparing standard solutions.

**How to use a measuring flask :**

(*i*) Rinse the flask with cleaning solution (chromic acid) ; wash it with tap water several times and finally with distilled water.

(*ii*) Pour the solution or solid by means of a funnel.

(*iii*) Wash the funnel thoroughly with cleaning solution and distilled water. Allow the washings to go into the flask. Shake the contents well.

(*iv*) Remove the funnel. Now add sufficient distilled water to near the graduation mark.

(*v*) Now add water drop by drop with a pipette until the lower meniscus of the solution touches the graduation mark. Observe this at eye-level to avoid errors due to parallax.

(*vi*) Stopper the flask and invert it several times so as to produce a homogeneous solution.

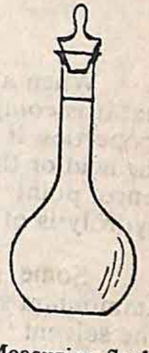
**Precautions to be observed while using a measuring flask**

(*i*) Rinse the flask thoroughly with cleaning solution. Now wash with tap water followed by distilled water.

(*ii*) Always use funnel to transfer solution to the measuring flask and do not allow the funnel to rest on the neck of the latter.

(*iii*) Wash the funnel with distilled water before removing it from the measuring flask.

(*iv*) Measuring flask should never be heated. Never place hot solution into it.



Measuring flask
Fig. 9.10

(*v*) Its stopper should not be changed.

(*vi*) It should not be rinsed with solution to be stored in it.

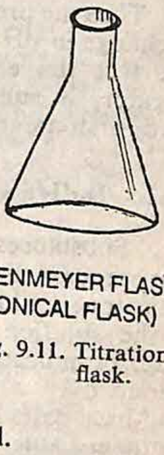
**Titration flask.** It is a small flat-bottomed flask with a wide neck and large belly. The wide neck permits the flow of the solution from the burette while the flask is swirled when carrying out the titration. Conical flasks are best suited for the purpose, as they can be heated conveniently as and when required (Fig. 9.11).

**How to use a titration flask** :

(*i*) Clean the titration flask with chromic acid and tap water followed by distilled water.

(*ii*) The required volume of the solution is taken into it with the help of a pipette.

(*iii*) After each titration, it should be cleaned and washed thoroughly with distilled water.



ERLENMEYER FLASK
(CONICAL FLASK)

Fig. 9.11. Titration flask.

(*iv*) Never rinse it with the solution to be titrated.

## 9.4. Acid-Alkali Titration (Acidimetry or Alkalimetry)

By acidimetry, we mean the determination of unknown strength of an alkali by titration with a standard solution. Alkalimetry is just the opposite of this statement. When an acid is mixed with an alkali, $H^+$ ions of the acid react with $OH^-$ ions of the alkali to produce water. The solution can therefore be either acidic (when an excess of $H^+$ ions are present) or alkaline (when an excess of $OH^-$ ions are present) or neutral (pH of the solution 7 ; neither the $H^+$ ions nor the $OH^-$ ions are present in excess desired by the equivalence point). For example, in the reaction of HCl (a strong acid) with NaOH (a strong base), the condition of neutrality is reached.

$$Na^+(aq)+OH^-(aq)+H^+(aq)+Cl^-(aq) \longrightarrow Na^+(aq)+Cl^-(aq)+H_2O(l)$$

The net change is

$$H^+(aq)+OH^-(aq) \longrightarrow H_2O(l)$$

When a certain amount of an acid is so treated with an alkali that it is completely converted into a normal salt and loses its acidic properties, it is said to be neutralized. The case is otherwise when the acid or the base or both are weak. The solution at the equivalence point will be either acidic or alkaline. This is due to the hydrolysis of the salt produced in the neutralization reaction.

Some salts are able to act as acids or bases, for example, ammonium salts are acidic, the ammonium ion yielding a proton to the solvent:

$$NH_4^+(aq)+H_2O(l) \rightleftharpoons NH_3(aq)+H_3O^+(aq)$$

Carbonates abstract protons from the solvent and so act as bases:

$$CO_3^{2-}(aq)+H_2O(l) \rightleftharpoons HCO_3^-(aq)+OH^-(aq)$$

Thus the progress of any acid-base titrations would be to monitor the change in pH with an electrical pH meter. But it is customary to detect the end point of a titration with the aid of chemical indicator, a substance which changes colour when the pH of its solution alters.

### 9.4.1. Indicators and end point

Substances which can indicate the termination of a neutralization process by change of colour are called indicators. A good indicator should give a sharp change of colour when the condition of the solution changes from acidic to alkaline and vice-versa. A range of indicators is available for titrations. Each indicator changes colour over a range of pH. Indicators are themselves conjugate acid-base pairs in which the acid form and the basic form are clearly distinguishable by eye. Every indicator has its **working range** (range of pH over which the colour changes). Choice of indicators in neutralization reactions depends upon the nature of the acids and bases and also on their concentrations. For a titration to be feasible, there should be a satisfactory change of pH at or near the equivalence point by adding a small volume of acid or alkali. Hence, indicator that changes colour at or near the equivalence point should be chosen. Now by the use of an indicator one can know what volume of an acid solution will exactly react with a given volume of an alkali. The colour change of the indicators gives the termination point of the titration, and hence, the end point. In acid-alkali titrations the indicator is usually one of the listed in Table 9.1.

**Table 9.1. Choice of indicators**

| *Type of titration* | *Indicator* | *Alkaline Solution* | *Neutral Solution* | *Acidic Solution* |
|---|---|---|---|---|
| 1. Hydrochloric acid —caustic soda (Strong acid— strong base) | Any indicator with a colour change between pH 3 and 10 | — | — | — |
| 2. Acetic acid— caustic soda (Weak acid— strong base) | Phenolphthalein | Red | Pink | Colourless |
| 3. Ammonia— sulphuric acid (Weak base— strong acid) | Methyl orange | Yellow | Orange | Red |
| 4. Ammonia— hydrochloric acid (Weak base— strong acid) | Screened methyl orange | Green | Green | Red |
| 5. Acetic acid— ammonia (Weak acid— weak base) | No satisfactory end point can be obtained by using any indicator. Such a titration should be avoided. | | | |

In practice, when a strong acid and a strong base are being used the pH change at the end point is so large that virtually any indicator is likely to be satisfactory ; when a weak acid is being titrated with a strong base it is necessary to use an indicator which changes colour on the alkaline side of pH 7 ; phenolphthelein is a suitable indicator in this case and when a strong acid is being titrated with a weak base it is necessary to use an indicator which change colour on the acid side ; suitable indicator of this titiation would be methyl orange and bromocresol green.

When sodium carbonate is reacted with hydrochloric acid, two reactions occur :

$$Na_2CO_3+HCl \longrightarrow NaCl+NaHCO_3$$

and

$$Na_2CO_3+2HCl \longrightarrow 2NaCl+CO_2+H_2O$$

The first reaction is complete at a high pH and so can be followed by phenolphthalein. The second reaction has an point at a low pH and is indicated by methyl orange.

### 9.4.2. Calculations

Titration calculations can be reduced to a few simple steps. It is essential to know which substance is acting as the standard. The steps required are : (1) the determination of equivalent mass of the standard used on the basis of balanced chemical equation ; (2) the calculation of the normality of the standard solution ; (3) the calculation of the normality of the other solution ; and (4) the determination of the quantity (concentration, purity, etc.) required.

## Normality equation

Since neutralization is the reation between equivalents of $H^+(aq)$ and $OH^-(aq)$ to form water, it is desirable to use normal concentrations rather than molar concentrations. While a litre of 1·0 *M* NaOH solution will not neutralize a litre of 1·0 *M* $H_2SO_4$ solution, equal volumes of 1·0 *N* solutions of any acid or base, will neutralize each other. Since one mole of $H_2SO_4$ can produce two moles of $H^+(aq)$ a half-mole of $H_2SO_4$ (the equivalent mass) produces 1 mole of $H^+(aq)$ :

$$\begin{array}{lll} H_2SO_4 \longrightarrow & 2H^+ + & SO_4^{2-} \\ 1 \text{ mole} & 2 \text{ mole} & 1 \text{ mole} \\ \frac{1}{2} \text{ mole} & 1 \text{ mole} & \frac{1}{2} \text{ mole} \end{array}$$

In effect, neutralization occurs when the number of equivalent's of acid equals the number of equivalents of base.

Number of equivalents of acid = Number of equivalents of base

Accordingly if the solution of a substance A is titrated against the solution of a substance B then at the end point we can write as follows :

Number of gram-equivalents of solution A

= Number of gram-equivalents of solution B

or
$$N_1V_1 = N_2V_2 \tag{9.1}$$

where $N_1$ and $N_2$ are the normalities and $V_1$ and $V_2$ the volumes of solutions A and B respectively.

From Eq. (9.1), the normality of a unknown solution can be calculated. Let this be $x$. Now $N_1V_1 = N_2V_2$. If $N_1$, $V_1$ and $V_2$ are known, $N_2 = x$ can be calculated by the equation

$$N_2 = \frac{N_1V_1}{V_2} \tag{9.2}$$

## Calculation of strength (concentration)

With the known/calculated normality of a solution, its strength in grams per litre can be known by applying the following relation :

$$\text{Strength} = \text{Normality} \times \text{Equivalent weight} \tag{9.3}$$

## Calculation of equivalent weight

With the strength and normality of a solution of a substance, the equivalent weight of the substance dissolved (solute) can be calculated by applying the following equation :

$$\text{Equivalent weight of the solute } (E) = \frac{\text{Strength } (S)}{\text{Normality } (N)}$$

or
$$E = \frac{S}{N} \tag{9.4}$$

**Calculation using molarity**

The steps required are :

(1) The determination of the number of moles of the standard used ; (2) the writing of a balanced chemical equation ; (3) the calculation of the number of moles of the other compound ; (4) the conversion of the number of moles of the other compound to a mass ; and so (5) the determination of the quantity (concentration, purity, etc.) required.

It may be recalled that the molar solution of a substance is that solution which contains one gram molecular weight (or one mole) of it per litre of the solution.

For example, the molecular weight of HCl is 36·5. Thus, a solution containing 36·5 g of hydrochloric acid in one litre of solution will be 1 *M*. Similarly when 3·65 or 0·73 g of it are present in one litre, the molarity of the solutions will be 0·1 *M* or *M*/10 and 0·02 *M* or *M*/50 respectively. Mathematically molarity may be expressed as given below :

$$M=\frac{\text{Number of moles of solute}}{\text{Volume in litre}}$$

$$=\frac{\text{Weight of solute in g L}^{-1}}{\text{Molecular weight of the solute}}$$

$$=\frac{\text{Weight of the solute in grams}}{\text{Molecular weight of solute}\times\text{Volume of solution in litre}}$$

Thus, using above relationship, the molarity of a solution can be determined if the molecular weight of the solute and the amount dissolved per litre of the solution is known. Also, the amount of solute which is to be dissolved (for preparing a solution of known molarity) can be computed from the above relationship.

Weight of solute (in grams) = Molecular weight of the solute × Volume of solution in litre × molarity

**Relationship between normality and molarity.** The concentration terms, molarity and normality can be inter-related to each other by a simple relationship given below :

Normality = Molarity × number of equivalents per molecular weight of the solute

$$=\text{Molarity}\times\frac{\text{Molecular weight}}{\text{Equivalent weight}}$$

= Molarity × Number of electrons gained or lost per molecule (or ion) of the solute in balanced equation

$$N=M\times n$$

where $n$ = Number of electrons gained or lost per molecule (or ion) in balanced equation.

### 9.4.3. Conditions for volumetric analysis

Estimation by volumetric analysis is feasible only if the reaction involved fulfills the following conditions :

(*i*) The reaction must take place till completion and instantaneously.

(*ii*) The end point should coincide with the equivalence point.

(*iii*) There should be no side reactions.

(*iv*) The reaction should be specific.

(*v*) The reaction involved should be definite. It should be represented by a chemical equation.

(*vi*) The end point should be definite, either between the reacting substances or by the use of an indicator.

### 9.4.4. Preparation of the standard solution

A solution of known concentration is considered as a standard solution. Some of the standard solutions are prepared by weighing out accurately and dissolving the weighed solute in a suitable solvent and making up the solution to a known volume. Such solutions of known concentrations are called primary standard solutions as other solutions are standardized against them. The procedure for preparing such solutions has already been given in section 1.20.1 (Unit 1).

#### Weights required for some of the primary standard substances

#### (*i*) For 0·1 *N* sodium carbonate solution

Equivalent weight of $Na_2CO_3$ is 53 g/eq, 5·3 g of $Na_2CO_3$ would be required for 1 litre *N*/10 $Na_2CO_3$ solution. In the laboratory, generally 250 ml of the solution is prepared. Therefore, to prepare 250 ml of *N*/10 $Na_2CO_3$, 5·3 g/4=1·325 g of $Na_2CO_3$ is required.

#### (*ii*) For 0·1 *N* oxalic acid solution.

Equivalent weight of oxalic acid is 126/2=63. Thus, to prepare 1 litre 0·1 *N* solution of oxalic acid we would require 6.3 g. To prepare 250 ml of *N*/10 solution of oxalic acid, we would require $\frac{63}{10\times4}$ g=1·575 g.

#### (*iii*) For 0·1 *M* sodium carbonate solution

Molecular mass of anhydrous sodium carbonate is 106 g. To prepare 1 litre 0·1 *M* sodium carbonate solution the weight of sodium carbonate required would be :

Weight of sodium carbonate = Molecular mass of sodium carbonate × Volume of solution × molarity

$$=106\ \text{g}\times1\ \text{L}\times(1/10)=10{\cdot}6\ \text{g/L}$$

In laboratory, generally 250 ml of the solution is prepared. Therefore, the weight required would be equal to 10·6/4 g, *i.e.* 2·65 g (or 0·1 *N*).

(*iv*) **For 0·1 *M* sodium bicarbonate solution**

Molecular wt. of sodium bicarbonate=84 g

To prepare 1 litre 0·1 *M* sodium bicarbonate solution, the weight of sodium bicarbonate required would be :

=Molecular weight of $NaHCO_3$ × Volume of solution × Molarity

$$=84\text{ g}\times 1\text{ L}\times \frac{1}{10}=8{\cdot}4\text{ g/L}$$

To prepare 1 litre solution of 0 1 $M$=8·4 g

To prepare 250 ml solution of 0·1 $M$=2·1 g

To prepare 250 ml solution of 0·1 $N$=2·1 g

(*v*) **For 0·1 *M* and 0·1 *N* oxalic acid solution**

Molecular weight of oxalic acid=126 g

To prepare 1 litre 0·1 *M* oxalic solution, the weight of oxalic acid required would be

=Molecular mass of oxalic acid × Volume of solution × Molarity

$$=126\text{ g}\times 1\text{ L}\times \frac{1}{10}=12{\cdot}6\text{ g/L}$$

Amount of oxalic acid required for one litre 0·1 *M* solution =12·6 g

Amount of oxalic acid required for 250 ml 0·1 *M* solution =3·15 g

Amount of oxalic acid required for 250 ml 0·1 *N* solution =1·575 g

$$\left(\because\ \text{Eq. wt.}=\frac{\text{Mol. wt.}}{2}\right)$$

## 9.5. Experiments

**Experiment 9.1.** To prepare 250 ml 0·1 *N* HCl solution (given 0·1 *N* $Na_2CO_3$ solution).

**Theory.** The concentrated HCl available from the market is roughly 12 *N*. It is volatile in nature so it is not possible to prepare a standard solution by measuring out a definite volume and then diluting it. A solution of approximate strength is prepared and then standardized by titrating against standard $Na_2CO_3$ solution.

**Procedure**

(*i*) **Preparation of approximately 0·1 $N$ HCl solution, 250 ml.** Measure out 2·5 ml of pure conc. HCl with the help of a 10 ml measuring cylinder and pour slowly into a 500 ml beaker containing about 200 ml distilled water. Stir the solution with a glass rod and dilute it to about 250 ml by adding more of distilled water.

(*ii*) **Titration.** Rinse and fill the burette with dilute HCl acid solution. Record the initial reading of the burette. Pipette out standard solution of given 0·1/$N$ $Na_2CO_3$ solution into a clean conical flask. Add 2 drops of methyl orange and titrate it against the acid with constant stirring until a permanent pink colour is obtained. Run the HCl solution slowly, in small amounts at a time and take the final reading by noting down the lower meniscus only. Repeat the titration to obtain at least three concordant readings.

**Indicator : Methyl orange**

**Normality of the $Na_2CO_3$ solution : 0·1 $N$.**

**Observations**

| *S.N.* | *Volume of $Na_2CO_3$ solution taken in a conical flask* | *Initial burette reading* | *Final burette reading* | *Difference : Volume of acid consumed ($V$ ml)* | |
|---|---|---|---|---|---|
| 1. | 20 ml | ...ml | ...ml | | |
| 2. | 20 ml | ...ml | ...ml | 18 ml | Three concordant readings |
| 3. | 20 ml | ...ml | ...ml | 18 ml | |
| 4. | 20 ml | ...ml | ...ml | 18 ml | |

**Calculations**

Suppose 20 ml of 0·1 $N$ $Na_2CO_3$ requires 18 ml HCl solution

$$20\times\frac{N}{10}=18\times N\ \text{HCl}$$

$$\text{Normality of HCl solution}=\frac{20\times0{\cdot}1\ N}{18}=0{\cdot}11\ N$$

(*iii*) **Preparation of exact 0·1 $N$ HCl solution.** Normality of the experimentally prepared HCl solution is 0·11 $N$ (a little more concentrated than actually required). Now this has to be diluted until the solution of desired normality is obtained. The volume of solution to be diluted to a known volume of 0·1 $N$ is calculated from the normality equation.

$$N_1V_1=N_2V_2$$

where $N_1$=original normality ; $V_1$=original volume to be taken

$N_2$=required normality ; $V_2$=volume after dilution

$$\therefore \quad V_2=\frac{N_1V_1}{N_2}.$$

Now the volume of distilled water to be added to the $V_1$ ml of HCl is equal to $(V_2-V_1)$ ml.

In the present case

$N_1=0{\cdot}11\ N$ ; $V_1=?$

$N_2=0{\cdot}1\ N$ ; $V_2=250$ ml, the volume to be prepared

$$0{\cdot}11\ N\times V_1=0{\cdot}1\ N\times 25$$

$$V_1=\frac{0{\cdot}1\ N\times 250}{0{\cdot}11\ N}=227{\cdot}3 \text{ ml}$$

Hence 227·3 ml of HCl solution is taken in a measuring flask and the solution is made up to the graduation mark with distilled water.

**Experiment 9.2.** To prepare a standard 0·1 *N* NaOH solution (given 0·1 *N* HCl solution).

**Procedure**

(*i*) **Preparation of approximately 0·1 *N*-NaOH solution.** Weigh out about 1·4 to 1·5 g of NaOH pellets. Wash the pellets with 2-3 ml distilled water and throw the washing. (This will dissolve the sodium carbonate formed on the surface.) Now take the remaining part in a beaker and dissolve in 200 ml distilled water. Allow the solution to cool. Now add 50 ml more of water to make 250 ml solution. Stir it well to get a homogeneous solution. This resultant solution is approximately 0·1 *N* NaOH.

(*ii*) **Titration.** Rinse and fill the burette with standard HCl solution. Recored the initial burette reading by noting the bottom of the menisucus. Pipette out 20 ml NaOH solution into a clean conical flask. Add 2 drops of phenolphthalein. Run the acid solution slowly from the burette until the solution in the flask becomes just colourless. Note the final burette reading. Repeat the titration to obtain at least three *concordant readings*.

**Indicator : Phenolphthalein**

**Normality of HCl solution used=0·1 *N***

**Observations**

| *S.N.* | *Volume of NaOH solution taken in a conical flask* | *Initial burette reading* | *Final burette reading* | *Volume of HCl solution consumed (V ml)* | |
|---|---|---|---|---|---|
| 1. | 20 ml | ...ml | ...ml | | |
| 2. | 20 ml | ...ml | ...ml | 22 ml | Three concordant readings |
| 3. | 20 ml | .. ml | ...ml | 22 ml | |
| 4. | 20 ml | ...ml | ...ml | 22 ml | |

**Calculation**. Suppose 20 ml of NaOH solution requires 22 ml of 0·1 $N$ HCl solution.

$$\text{Normality of NaOH solution} = \frac{22}{20} \times 0{\cdot}1\ N$$
$$= 0{\cdot}11\ N$$

(*iii*) **Preparation of exact 0.1 N NaOH solution**. The volume of NaOH (0.11 $N$) solution required to prepere 250 ml of 0.1 $N$ NaOH solution is calculated as given below :

$N_1 = 0{\cdot}11\ N$ ; $V_1 = ?$

$N_2 = 0{\cdot}1\ N$ ; $V_2 = 250$ ml, the volume to be prepared

Now $0{\cdot}11\ N \times V_2 \equiv 0{\cdot}1\ N \times 250\ \text{ml}$

or $$V_1 = \frac{0{\cdot}1\ N \times 250\ \text{ml}}{0{\cdot}11\ N} = 227{\cdot}3\ \text{ml}$$

Hence, 227·3 ml of NaOH (0·11 $N$) is taken into a 250 ml measuring flask and the solution is made up to the graduation mark with distilled water.

**Note**. KOH solution is also standardized in a similar way.

**Experiment 9.3**. To determine the strength in grams per litre of NaOH solution by titrating it against standard solution of oxalic acid.

**Theory**. Sodium hydroxide solution is titrated against standard oxalic acid solution using phenolphthalein as an indicator. The strength of the alkali is later calculated from the data gathered.

**Procedure**. (*i*) Prepare 0·1$N$ standard oxalic acid solution by weighing out 1·575 g oxalic acid and dissolving in 250 ml measuring flask and finally making up the solution to the graduation mark.

(*ii*) Rinse and fill the burette with sodium hydroxide solution. Pipette out 20 ml standard oxalic acid solution in a clean conical flask. To it add two drops of phenolphthalein and titrate it against the alkali with constant stirring until a permanent pink colour is obtained. Repeat the titration to get three concordant readings. Record your observations as tabulated below :

**Indicator used : Phenolphthalein**

**Normality of the standard oxalic acid solution : 0·1 $N$**

**Observations**

| *S.N.* | *Volume of oxalic acid solution taken in a conical flask* | *Initial burette reading* | *Final burette reading* | *Volume of NaOH solution consumed (V ml)* | |
|---|---|---|---|---|---|
| 1. | 20 ml | ...ml | ...ml | | |
| 2 | 20 ml | ...ml | ...ml | 18 ml | Three concordant readings |
| 3. | 20 ml | ...ml | ...ml | 18 ml | |
| 4. | 20 ml | ...ml | ...ml | 18 ml | |

### Calculations

Suppose 20 ml 0·1 $N$ oxalic acid solution requires 18 ml of NaOH solution

$$\text{Normality of NaOH solution}=\frac{20\times 0{\cdot}1\ N}{18}=0{\cdot}11\ N$$

Strength of NaOH solution = Normality × Equivalent weight of NaOH

$$\text{Strength of NaOH solution}=0{\cdot}11\times 40\ \text{g/L}$$
$$=4{\cdot}4\ \text{g/L}$$

**Result**. The strength of the given NaOH solution is 4·4 g/L

**Experiment 9.4**. To determine the strength of given hydrochloric acid solution in grams per litre by titrating it against standard sodium carbonate solution.

**Theory**. In this case HCl solution is titrated against standard sodium carbonate solution using methyl orange or phenolphthalein as the indicator. When acid is taken in the burette, methyl orange is used as indicator and when alkali is taken in the burette, phenolphthalein is used as indicator.

**Note**. Here we will do the titration using methyl orange as an indicator. Use of phenolphthalein as indicator will be discussed in experiment 9.5.

**Procedure**. (*a*) Prepare $N/10$ standard sodium carbonate solution by weighing out 1·325 g $Na_2CO_3$ and dissolving it into a 250 ml measuring flask and finally making up the solution to the graduation mark.

(*b*) Rinse and fill the burette with hydrochloric acid solution. Pipette out 20 ml of $N/10$ standard $Na_2CO_3$ solution in a clean conical flask. To it add two drops of methyl orange and titrate it against the acid with constant stirring until a permanent pink colour is obtained. Repeat the titration to obtain at least three concordant readings.

Record your observations as tabulated below :

**Indicator used : Methyl orange**

**Normality of $Na_2CO_3$ solutions 0·1 $N$**

**Observations :**

| *S.N.* | *Volume of $Na_2CO_3$ solution taken in a conical flask* | *Initial burette reading* | *Final reading burette* | *Volume of oxalic acid solution consumed ($V$ ml)* | |
|---|---|---|---|---|---|
| 1. | 20 ml | ...ml | ...ml | | |
| 2. | 20 ml | ...ml | .. ml | 25 ml | Three concordant readings |
| 3. | 20 ml | ... ml | ...ml | 25 ml | |
| 4. | 20 ml | ...ml | ...ml | 25 ml | |

**Calculations** : Suppose 20 ml of 0·1 $N$ $Na_2CO_3$ solution requires 25 ml of HCl solution.

$$\text{Normality of HCl solution} = \frac{20 \times 0{\cdot}1\ N}{25} = 0{\cdot}08\ N$$

Strength of hydrochloric acid solution

$$= \text{Normality} \times \text{Equivalent weight of HCl}$$

$$\text{Strength of HCl} = 0{\cdot}80 \times 35{\cdot}5 \text{ g/L}$$

$$= 2{\cdot}84 \text{ g/L}$$

**Result.** The strength of the given HCl solution is 2·84 g/L

**Experiment 9.5**. To determine the strength of a given HCl solution in grams per litre by titrating against sodium hydroxide solution or sodium carbonate solution.

**Procedure**. The solution of sodium hydroxide is standardized by using a standard solution of oxalic acid. Use 1·575 g oxalic to prepare 250 ml of $\frac{N}{10}$ solution. Oxalic acid is taken in a conical flask to which 2 drops of phenolphthalein are added. Allow the titrant (NaOH) to run into the flask until the solution acquires pink colour. Find the volume of sodium hydroxide solution used. Calculate the normality of NaOH solution.

Now allow the NaOH solution (normality has been found, hence standard solution) to run into a flask containing HCl solution to which two drop of phenolphthalein have been added. Continue to add titrant until the solution acquires permanent colour. Record your observations and do the calculation as given under Experiment 9.4.

Now with a standard solution of $Na_2CO_3$ in burette use phenolphthalein as indicator and repeat the titration procedure.

**Exercise 9.1.** 0·125 $M$ hydrochloric acid is prepared by diluting 12 ml of concentrated hydrochloric acid to exactly 1 litre solution. Calculate the molarity of the concentrated acid.

**Solution.** Molarity of concentrated acid

$$= \text{Molarity of diluted acid} \times \frac{\text{Volume of diluted acid}}{\text{Volume of concentrated acid}}$$

$$= 0{\cdot}125 \times \frac{1000}{12} M$$

$$= 10{\cdot}42\ M$$

The concentrated hydrochloric acid is 10·42 $M$.

**Exercise 9.2.** 20 ml of 0·1 $M$ nitric acid neutralizes 21 ml of sodium carbonate solution. Calculate the concentration of the carbonate in g/L of solution.

**Solution**. The equation for the reaction is :

$$\underset{\substack{2000\text{ ml}\\1\ M\text{-acid}}}{2\,HNO_3} + \underset{\substack{1000\text{ ml}\\1\ M\text{ carbonate}}}{Na_2CO_3} \longrightarrow 2NaNO_3 + CO_2 + H_2O$$

$$\frac{\text{(Molarity} \times \text{Volume) of acid}}{\text{(Molarity} \times \text{Volume) of carbonate}} = \frac{1 \times 2000}{1 \times 1000} = \frac{2}{1}$$

$$\frac{0{\cdot}1 \times 20}{\text{Molarity of carbonate} \times 21} = \frac{2}{1}$$

$$\text{Molarity of carbonate} = \frac{0{\cdot}1 \times 20}{2 \times 21}$$

$$= 0{\cdot}0476\ M$$

One mole of sodium carbonate contains 106 g

∴ One molar $Na_2CO_3$ solution contains 106 g/L

∴ 0·0476 $M$ $Na_2CO_3$ solution contains 0·0476 × 106 g/L
=5·04 g/L

The concentration of sodium carbonate solution is 5·04 g/L

**Exercise 9.3**. 20 ml of 0·1 $M$ $H_2SO_4$ neutralizes 22·5 ml of $Na_2CO_3$ solution. Calculate the molarity and concentration of the $Na_2CO_3$ solution in g/L.

**Solution.** The equation for the reaction is :

$$\underset{\substack{1000\text{ ml} \\ M\text{-acid}}}{H_2SO_4} + \underset{\substack{1000\text{ ml} \\ M\text{-acid}}}{Na_2CO_3} \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$\therefore \quad \frac{\text{(Molarity} \times \text{Volume) of carbonate}}{\text{(Molarity} \times \text{Volume) of acid}} = \frac{1 \times 1000}{1 \times 1000} = \frac{1}{1}$$

$$\frac{\text{(Molarity of carbonate)} \times 22{\cdot}5}{0{\cdot}1 \times 20} = \frac{1}{1}$$

$$\text{Molarity of carbonate solutlon} = \frac{0{\cdot}1 \times 20}{22{\cdot}5}$$

$$= 0{\cdot}0888\ M$$

One mole of sodium carbonate contains 106 g

∴ One molar $Na_2CO_3$ solution contains 106 g in 1 litre of solution.

∴ 0·0888 $M$ $Na_2CO_3$ solution contains 0·0888 × 106 g of $Na_2CO_3$ in 1 litre solution=9·32 g/L.

The concentration of sodium carbonate solution is 9·32 g/L.

## ORAL QUESTIONS AND ANSWERS

**Q. 9.1.** What do you mean by volumetric analysis ?

**Ans**. The analysis which involves exact measurment of volume titre and titrant is termed as volumetric analysis.

**Q. 9.2.** What do you mean by titration ?

**Ans.** It is a process of running out a solution from a burette into a solution contained in a conical flask or a beaker until the reaction is complete. The completion of the reaction is monitored by the use of indicator or some other method.

**Q. 9.3.** What is an indicator ?

**Ans.** A substance used to determine the end point of a reaction is termed as indicator. It changes colour over a range of pH.

**Q. 9.4.** What is a standard solution ?

**Ans.** A solution of exactly known strength is called a standard solution.

**Q. 9.5.** What is a normal solution ?

**Ans.** A solution which contains one gram equivalent weight of a solute dissolved per litre of the solution is termed as normal solution.

**Q. 9.6.** What is normality equation ?

**Ans.** According to the law of equivalents the number of equivlents of an substance (say acid) reacts with the equal number of equivalents of another substance (say base).

Therefore, $N_1V_1=N_2V_2$

This is called the normality equation.

Refer to section 9.4.2.

**Q. 9.7.** Give helpful expressions used in volumetric analysis.

**Ans.** Equivalent weight of an acid $= \dfrac{\text{Molecular weight}}{\text{Basicity}}$

Equivalent weight of a base $= \dfrac{\text{Molecular weight}}{\text{Acidity}}$

$$\text{Strength} = \text{Normality} \times \text{Equivalent weight}$$

Also refer to section 9.4.2.

**Q. 9.8.** What is a titrant ?

**Ans.** The solution which is filled in the burette is called titrant. Usually its strength is known.

**Q. 9.9.** What is a titre ?

**Ans.** The solution which is kept in the conical flask for titration purposes. Its strength is normally to be determined.

**Q. 9.10.** What is an end point ?

**Ans.** The stage at which the colour change of the indicator is visible to the eye is called the end point.

**Q. 9.11.** What is a molal solution ?

**Ans.** A solution containing one mole of the solute per 1000 g of the solvent is called a molal solution.

**Q. 9.12.** What is a molar solution ?

**Ans.** A solution containing one mole of the solute per 1000 ml of the solution is called a molar solution.

**Q. 9.13.** What is a primary standard ?

**Ans.** A chemical substance which can be used directly for preparing the standard solution. It does not experience any chemical change at room temperature.

**Q. 9.14.** What is a decinormal solution ?

**Ans.** A $0{\cdot}1N$ solution is called a decinormal solution.

**Q. 9.15.** What is the strength of a solution ?

**Ans.** It is the quantity of a solute present in one litre of the solution. It is found out by the expression,

$$\text{Strength} = \text{Normality} \times \text{Equivalent mass}$$

It is expressed in g/L.

□ □

## UNIT 10

# Determination of Melting and Boiling Points of Organic Substances

### 10.1. Introduction

All substances have their distinctive physical and chemical properties. With the help of these properties one substance is distinguished from the other. Amongst the various properties melting or boiling point is also an important physical property. In the identification of organic compounds, the m.p. of the derivative prepared serves as the most important property in identifying the organic compound.

### 10.2. Melting Point

The melting point of a pure solid organic compound is used as a criteria of its purity because a pure organic solid always melts sharply at a definite temperature. Melting point is always lowered by the presence of impurities.

**Experiment 10.1.** To determine the melting point of organic compounds.

**Apparatus and Chemicals**. A pyrex beaker or a wide mouth boiling tube, thermometer, solvent (water or paraffin oil), tripod stand, clamp, wire gauze, glass capillary, organic compounds etc.

**Procedure**. Determination of melting point of an organic compound may be divided into two parts :

(*a*) filling of the capillary tube,

(*b*) determinution of melting point.

(*a*) **Filling of the capillary tube**

(*i*) Powder the organic compound in a mortar whose m.p. is to be determined or in a porous plate with the help of a spatula [Fig. 10.1 (A)].

(*ii*) Take a fine capillary tube (about 4 cm long). Seal its one end by bringing it near the flame of the burner for a few seconds. The glass becomes red hot and on cooling the mouth of the capillary closes.

(*iii*) Hold the capillary between the fingers of the right hand and bring the open end of the capillary near the powdered heap of the compound. Some of the substance will enter into the capillary tube [Fig. 10.1 (B)].

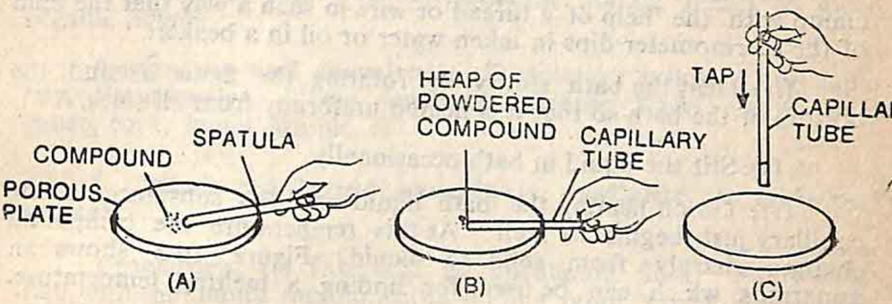


Fig. 10.1. Filling of capillary tube

(*iv*) Now hold the capillary with its sealed end down between thumb and a finger. Tap your hand against the table. The powder will go near the close end [Fig. 10.1 (C)].

(*v*) Repeat the steps (*iii*) and (*iv*) to fill the capillary to a capacity of ½ cm in length.

### (*b*) Determination of melting point

(*i*) Take a beaker and fill it half with water (when the m.p. is below 90°C) or with paraffin oil (when the m.p. is above 90°C). This will work as the heating bath. Put a stirrer into it.

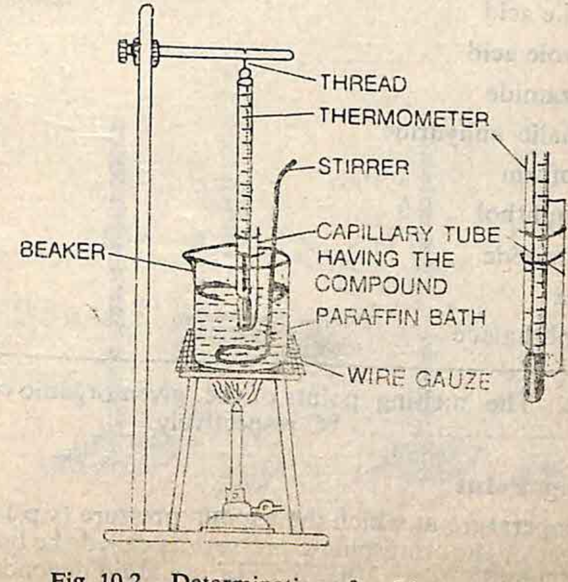


Fig. 10.2. Determination of melting point.
[The open end of the capillary must be kept above the liquid level and the thermometer should not touch the side wall or the bottom of the bath].

(*ii*) Attach the capillary tube to the bulb of the themometer either with an asbestos thread or a rubber band so that the closed end of the capillary sticks to the bulb of the thermometer.

(*iii*) Suspend the thermometer alongwith capillary from the clamp with the help of a thread or wire in such a way that the bulb of the thermometer dips in taken water or oil in a beaker.

(*iv*) Heat the bath slowly by rotating the flame around the bottom of the bath so that it is heated uniformly from all sides.

(*v*) Stir the liquid in bath occasionally.

(*vi*) Go on heating the bath liquid until the substance in the capillary just begins to melt. At this temperature the compound changes sharply from solid to liquid. Figure 10.2 shows an apparatus which can be used for finding a melting temperature. Record this temperature.

**Note.** The presence of impurity lowers the melting temperature, and also results in a more gradual melting over a range of temperature.

**Observations**

| *S. N.* | *Organic Compound* | *Determined m.p. (°C)* | *Literature m.p. (°C)* |
|---|---|---|---|
| 1. | Acetanilide | | 114 |
| 2. | Oxalic acid | | 101 |
| 3. | Benzoic acid | | 121 |
| 4. | Benzamide | | 128 |
| 5. | Phthalic anhydride | | 128 |
| 6. | Iodoform | | 119 |
| 7. | α-Naphthol | | 94 |
| 8. | Acetomide | | 82 |
| 9. | Urea | | 132 |
| 10. | Naphthalene | | 80·2 |

**Result.** The melting points of the given organic compounds ............are ...................... °C respectively.

## 10.3. Boiling Point

The temperature at which the vapour pressure (v.p.) of a liquid is equal to that of the atmospheric pressure is called the boiling point (b.p.) of that liquid. Since the b.p of a liquid depends upon the atmospheric pressure, it varies from place to place. The b.p.

of water at 1 atmospheric pressure is 100°C. It is lower at hills where the atmospheric pressure is low. The b.p. of a liquid increases in the presence of impurities present in the liquid. Boiling temperatures tend to be less reliable as a test of purity than melting temperatures because of the danger of superheating.

**Experiment 10.2.** To determine the boiling points of given organic liquids.

**Apparatus and chemicals.** Distillation flask of 25 ml capacity, thermometer, Liebig condenser, receiver flask, clamp, wire gauze, cork, liquid sample, etc.

(*a*) **When the liquid sample is available in sufficient quantity.**

**Procedure.** (*i*) Take a 25 ml distillation flask. Fill it about half with the liquid sample whose boiling point is to be determined. Fix up the thermometer as shown in Fig. 10.3. Now attach the Liebig condenser and a receiver flask as shown in Fig. 10.3. The bulb of the thermometer must be at the level of the side tube of the flask and should not touch the neck of the flask.

(*ii*) Heat the distillation flask gently and note down the temperature in the thermometer. The mercury in the thermometer will start rising and will become constant when whole of the liquid distills over.

(*iii*) Note this constant temperature. This is the boiling point of the liquid.

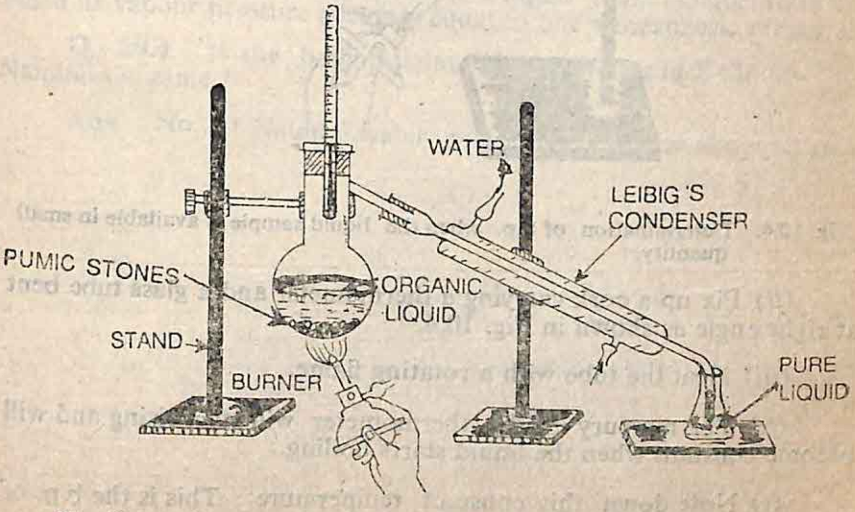


Fig. 10.3. Apparatus for the determination of boiling point of a liquid

(*iv*) When a boiling temperature is measured the thermometer must measure the temperature of the vapour in equilibrium with the boiling liquid (Fig. 10.3). It should not be immersted in the liquid because superheating (boiling above the boiling point) can occur if a liquid is heated rapidly.

**Note.** Boiling points of organic liquids (or inflammable liquids) are determined by distillation of the liquid (Fig. 10.3). For liquids boiling at higher than 100°C, air condenser is used.

### (*b*) When the liquid sample is available in small quantity.

**Procedure.** (*i*) Take a hard glass boiling tube and place a little of liquid sample in it. Put some pumic stones to avoid any spurting.

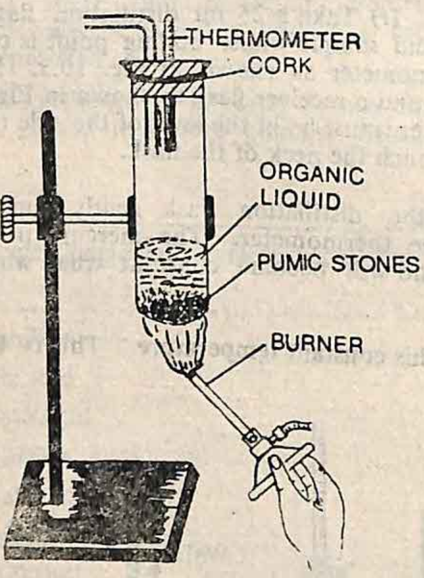


Fig. 10.4. Determination of b.p. when the liquid sample is available in small quantity.

(*ii*) Fix up a cork carrying a thermometer and a glass tube bent at right angle as shown in Fig. 10.4.

(*iii*) Heat the tube with a rotating flame.

(*iv*) The mercury in the thermometer will start rising and will become constant when the liquid starts boiling.

(*v*) Note down this constant temperature. This is the b.p. of the given liquid sample.

**Observations**

| *S. No.* | *Organic compound* | *Determined boiling point (°C)* | *Literature boiling point (°C)* |
|---|---|---|---|
| 1. | Benzene | | 80 |
| 2. | Acetone | | 56 |
| 3. | Acetic acid | | 118 |
| 4. | Carbon tetrachloride | | 77 |
| 5. | Ethyl alcohol | | 78 |

**Result.** The boiling points of the given liquids
.................... are ....................°C respectively.

## ORAL QUESTIONS AND ANSWERS

**Q. 10.1.** Define melting point.

**Ans.** When a pure solid substance is gradually heated, a temperature is reached at which it begins to melt. This temperature is called the *melting point* of the substance.

**Q. 10.2.** Define boiling point.

**Ans.** The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the pressure of the surrounding atmosphere.

**Q. 10.3.** Define normal boiling point of a liquid.

**Ans.** Normal boiling point of a liquid is the temperature at which its vapour pressure becomes equal to one atmospheric pressure.

**Q. 10.4**. Is the boiling point of pure water in Delhi and at Nainital the same ?

**Ans.** No. At Nainital water will boil at a higher temperature.

□ □

# UNIT 11

# Detection of Elements in Organic Compounds

## 11.1. Introduction

In organic compounds, the most commonly elements present are carbon, hydrogen, nitrogen, sulphur and halogens. In the identification of an organic compound, the first step is to detect the constituent elements. As carbon and hydrogen are found in almost all organic compounds these need not be detected. In order to detect the presence of nitrogen, sulphur and halogens, it is desired to convert them into ionizable inorganic substances. The Lassaigne test is performed for their detection. In this test, organic compounds are fused with sodium metal to convert the covalently bonded elements into anions. The sodium salts produced are water soluble ionic compounds. These can, therefore, be detected by employing the usual tests for anions.

## 11.2. Lassaigne Test for N, S and Halogens

(*i*) Take an ignition tube. It is made of soda glass which is easily fused.

(*ii*) Dry a pea size piece of freshly cut sodium metal by pressing between folds of filter paper. (Sodium metal is always kept in kerosene oil).

(*iii*) Introduce the dried pea size piece of sodium into the ignition tube and heat it gently over a Bunsen flame until the metal melts to a shining globule. Now cool the tube.

(*iv*) Now introduce a small quantity of organic compound (5-10 mg of solid ; 4-5 drops of liquid) into the ignition tube. This covers the sodium metal completely.

(*v*) Hold the ignition tube with the help of a pair of tongs and heat the ignition tube gently until the sodium fuses. Now heat it, first gently and then strongly, until reaction stops and the lower end of the ignition tube becomes red hot [Fig. 11.1(*a*)].

(*vi*) Plunge the hot ignition tube carefully into a porcelain dish containing about 10 ml of distilled water. Break the tube with a glass rod and the unreacted sodium, if any, undergoes reaction with water vigorously [Fig. 11.1(*b*)].

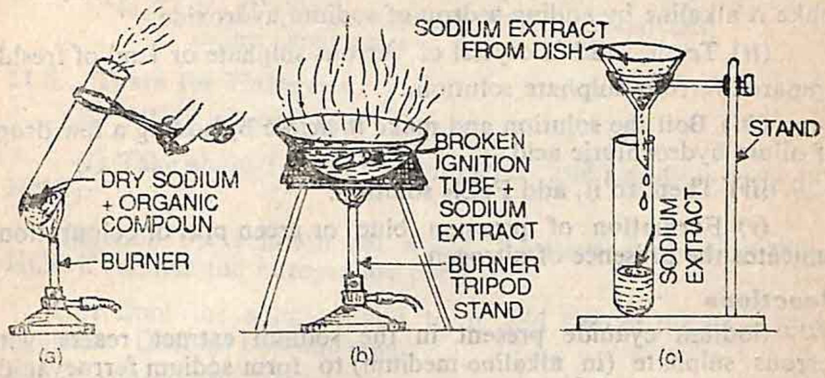


Fig. 11.1. Preparation of sodium extract

(*vii*) After the reaction is over, boil the contents of the dish for about 5 minutes and filter [Fig. 11.1(*c*)]. This is known as **sodium** or **soda extract.** Divide in into 5 parts.

**Reactions**

$$Na+C+\mathbf{N} \longrightarrow NaCN$$

$$Na+C+\mathbf{N}+\mathbf{S} \longrightarrow NaSCN$$

$$2Na+\mathbf{S} \longrightarrow Na_2S$$

$$Na+\mathbf{X} \longrightarrow NaX$$

$$(X=Cl,\ \mathbf{Br}\ 1)$$

The bold letters elements come from the organic compound.

**Precautions taken during preparation of soda extract**

(*i*) As sodium reacts vigorously with water, all the apparatus used during the fusion should be clean and perfectly dry.

(*ii*) While plunging the red-hot tube into cold water, the unreacted sodium may fly-off and cause damage. Therefore, while plunging the hot tube, cover the china dish with a wire guaze or watch glass.

(*iii*) In case the amount of compound taken is more than that of sodium or the heating is not done strongly, some compound remains unreacted or gets charred. The sodium extract thus obtained is dark coloured solution and the tests for different ions cannot be done. In such a case fresh sodium extract should be prepared by taking less amount of the compound and heating it strongly for a longer time.

## 11.3. Test for Nitrogen

(*i*) Take about 1 ml of the soda extract in a clean test-tube. Test it with a litmus paper for its alkalinity. If it is not alkaline, make it alkaline by adding a drop of sodium hydroxide.

(*ii*) To it, add a crystal of ferrous sulphate or 1 ml of freshly prepared ferrous sulphate solution.

(*iii*) Boil the solution and make it acidic by adding a few drops of dilute hydrochloric acid.

(*iv*) Then, to it, add $FeCl_3$ solution.

(*v*) Formation of prussian blue or green ppt. or colouration* indicates the presence of nitrogen.

**Reactions**

Sodium cyanide present in the sodium extract reacts with ferrous sulphate (in alkaline medium) to form sodium ferrocyanide which reacts with $Fe^{3+}$ ions (produced by the oxidation of $Fe^{2+}$ ions in air or extra added from the reagent bottle) to yield a blue or greenish blue colouration or ppt. of ferri-ferro cyanide.

$$\text{Na}+\underbrace{\text{C}+\text{N}}_{\substack{\text{(From organic}\\ \text{compound)}}} \xrightarrow{\text{Fuse}} \underset{\text{(In soda extract)}}{\text{NaCN}(aq)}$$

$$2NaCN+FeSO_4 \longrightarrow Fe(CN)_2+Na_2SO_4$$

$$4NaCN+Fe(CN)_2 \longrightarrow \underset{\text{Sodium ferro-cyanide}}{Na_4[Fe(CN)_6]}$$

$$4FeCl_3+3Na_4Fe(CN)_6 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3}+12NaCl$$

## 11.4. Tests for Sulphur

(*i*) Take 1 ml of sodium extract in a clean test tube. Acidify it with a few drops of dilute acetic acid. To it, add about 1 ml sodium acetate solution. Formation of a black precipitate indicates the presence of sulphur.

$$2Na+S\text{ (from organic compound)} \longrightarrow Na_2S(aq)$$

$$Na_2S+Pb(CH_3COO)_2 \longrightarrow \underset{\text{(Black ppt.)}}{PbS(s)}+2CH_3COONa$$

(*ii*) Take 1 ml of sodium extract in a clean test tube. To it, add a few drops of freshly prepared ammoniacal sodium nitroprusside

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*Formation of a blood red colouration indicates the presence of both N and S.

$$\text{Na}+\underbrace{\text{C}+\text{N}+\text{S}}_{\substack{\text{From organic}\\ \text{compound}}} \longrightarrow NaSCN$$

$$FeCl_3+3NaSCN \longrightarrow \underset{\substack{\text{Blood red colouration}\\ \text{also } Na_2[Fe(SCN)]}}{Fe(SCN)_3}+3NaCl$$

solution. Formation of a purple colour indicates the presence of sulphur in the given sample of a organic compound.

$$2Na + S \text{ (from organic compound)} \longrightarrow Na_2S(aq)$$

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{(Purple colour)}}{Na_4[Fe(CN)_5NOS]}$$

## 11.5. Tests for Halogens

### (1) Silver nitrate test

(*i*) Take about 1 ml of sodium extract and acidify it with dilute $HNO_3$.

(*ii*) Boil the solution for about 5 minutes to boil off $H_2S$ or HCN if sulphur and nitrogen are present.

(*iii*) Cool the solution and to it add 1 ml of the silver nitrate solution. Observe the following :

(*a*) Formation of a curdy white precipitate, soluble in ammonium hydroxide indicates the presence of chlorine in the organic compound.

(*b*) Formation of a light yellow precipitate, soluble to some extent in ammonium hydroxide indicates the presence of bromine in the organic compounds.

(*c*) Formation of a pale yellow precipitate insoluble in ammonium hydroxide indicates the presence of iodine.

**Reactions**

$$Na + X \text{ (from organic compound)} \longrightarrow NaX \text{ where } (X = Cl, Br, I)$$

(*a*)
$$NaCl + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCl(s)} + NaNO_3$$

(Soluble in aqueous ammonia)

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(Soluble complex)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

(*b*)
$$NaBr + AgNO_3 \longrightarrow \underset{\text{(Light yellow ppt.)}}{AgBr(s)} + NaNO_3$$

(Soluble to some extent in aqueous ammonia)

$$AgBr + 2NH_4OH \longrightarrow \underset{\text{(Sparingly soluble)}}{[Ag(NH_3)_2]Br} + 2H_2O$$

(*c*)
$$NaI + AgNO_3 \longrightarrow \underset{\text{(Yellow ppt.),}}{AgI(s)} + NaNO_3$$

(Insoluble in aqueous ammonia)

### (2) Carbon disulphide test (For Bromine and Iodine only)

(*i*) Take 1 ml of sodium extract in a clean test tube and acidify it with a few drops of dilute hydrochloric acid.

(*ii*) To it, add a few drops of fresh chlorine water and a few drops of carbon disulphide or carbon tetrachloride or chloroform.

(*iii*) Shake the contents vigorously and allow the two layers to separate.

(*a*) Appearance of orange or yellow colour in $CS_2$ layer indicates the presence of bromine.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + \underset{\text{(Extracted by organic solvent)}}{Br_2}$$

$$Br_2 + CS_2 \longrightarrow \text{Orange or yellow layer}$$

(*b*) Appearance of violet colour in $CS_2$ layer indicates the presence of iodine.

$$2I^- + Cl_2 \longrightarrow 2Cl^- + \underset{\text{(Extracted by organic solvent)}}{I_2}$$

$$I_2 + CS_2 \longrightarrow \text{Violet layer}$$

**(3) Beilstein Test**

This test is performed with the original compound as such. For this, heat tip of a clean copper wire in non-luminous flame until it ceases to impart any colour to the flame. Then dip the wire in the organic compound under examination, and again heat the tip of the wire strongly in flame. A green colour in the flame indicates the presence of halogens in the compound. This test does not differentiate between the three halogens. The test depends upon the volatility of copper halides.

**Note.** This test is also given by urea and thiourea which do not contain any halogen.

## ORAL QUESTIONS AND ANSWERS

**Q. 11.1.** Why is sodium metal kept in kerosene oil ?

**Ans.** It is always kept in kerosene oil, because it reacts with the atmospheric oxygen and also it reacts with water and its vapours.

**Q. 11.2.** Why can the elements like sulphur, nitrogen, bromine and iodine present in an organic compound not be tested like acid radicals ?

**Ans.** Organic compounds do not ionize in solution hence they cannot be tested like acid radicals.

**Q. 11.3.** What happens when an organic element is fused with sodium metal ?

**Ans.** Nitrogen, sulphur and halogens present in an organic compound are changed into soluble salts *e.g.*, NaCN, NaS and NaX etc.

**Q. 11.4.** Write down the complete reaction for the test of nitrogen.

**Ans.** The following chemical reactions occur while testing nitrogen.

$$Na + \underbrace{C + N}_{\substack{\text{(From organic}\\ \text{compound)}}} \xrightarrow{\text{Fuse}} \underset{\text{(In soda extract)}}{NaCN}$$

$$2NaCN + FeSO_4 \longrightarrow Fe(CN)_2 + Na_2SO_4$$

$$4NaCN + Fe(CN)_2 \longrightarrow Na_4[Fe(CN)_6]$$

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian Blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

**Q. 11.5.** What is Lassaigne extract ?

**Ans.** The fused mass produced by igniting an organic compound with sodium is extracted with hot water. A solution so produced is called Lassaigne or sodium extract.

**Q. 11.6.** What is the colour of the sodium extract ?

**Ans.** The sodium extract is colourless as its sodium salts are colourless.

**Q. 11.7.** Can we employ potassium for fusing an organic compound ?

**Ans.** Potassium is more active than sodium. It is likely to create difficulties during fusion, hence, it is not used.

**Q. 11.8.** Can we use tap water to prepare sodium extract ?

**Ans.** No, tap water should not be used as it contains $Cl^-$ ions. Only distilled water should be used for the purpose.

**Q. 11.9.** Why is fresh solution of ferrous sulphate used in the detection of nitrogen ?

**Ans.** Ferrous sulphate solution with time, gets oxidized to basic ferric sulphate by oxygen present in the atmosphere.

$$4FeSO_4 + 2H_2O + O_2 \longrightarrow \underset{\text{Basic ferric sulphate}}{4Fe(OH)SO_4}$$

**Q. 11.10.** The sodium extract of an organic compound gives a blood red colour with ferrous sulphate solution. Comment.

**Ans.** When nitrogen and sulphur are present in the organic compound, they on fusion form NaSCN which reacts with $Fe^{3+}$ ions to give a blood-red colour of ferrithiocyanate ion.

□ □

# UNIT 12

# Hydrocarbons

## 12.1. Introduction

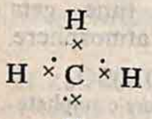
Hydrocarbons are the simplest organic compounds. They consist of only carbon and hydrogen atoms. Methane ($CH_4$), ethane ($C_2H_6$), propane ($C_3H_8$), ethylene ($C_2H_4$), acetylene ($C_2H_2$) and benzene ($C_6H_6$) are some of the examples of hydrocarbons.

Methane, ethane, ethylene, acetylene are *aliphatic* hydrocarbons whereas benzene is an *aromatic* hydrocarbon.

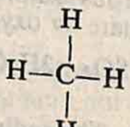
## 12.2. Alkanes

The alkanes constitute a family of hydrocarbons. The first member of this family is methane, $CH_4$. Second is ethane, $C_2H_6$. Propane, $C_3H_8$, is the third member of the alkane family. The electronic, structural and condensed structural formulae for methane, ethane and propane are given below :

Methane



Electronic formula

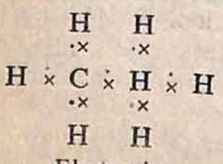


Structural formula

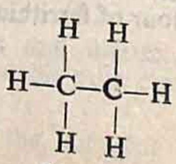
$CH_4$

Condensed structural formula

Ethane



Electronic formula

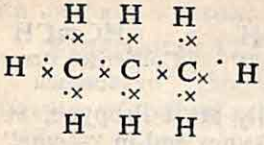


Structural formula

$H_3C—CH_3$

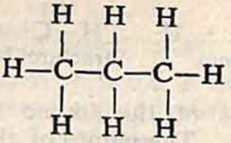
Condensed structural formula

Propane



$$\begin{array}{ccccccc} & & H & & H & & H \\ & & \cdot\times & & \cdot\times & & \cdot\times \\ H & \dot{\times} & C & \dot{\times} & C & \dot{\times} & C_{\times}\,\dot{}\,H \\ & & \cdot\times & & \cdot\times & & \cdot\times \\ & & H & & H & & H \end{array}$$

Electronic formula



$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C-H \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

Structural formula

$H_3C—CH_2—CH_3$

Condensed structural formula

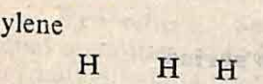
There are many more compounds in the alkane family. The names of all alkanes end in "——ane".

Alkane molecules are said to be **saturated.** In a saturated molecule, each carbon atom is bonded to four other atoms by single covalent bonds ; no double or triple bonds are present between carbon atoms. Saturated hydrocarbons are non-reactive. Hence saturated hydrocarbons are also called paraffins (para=less ; affins= affinity). The general formula of alkanes is $C_nH_{2n+2}$.

## 12.3. Alkenes (Olefins) and Alkynes

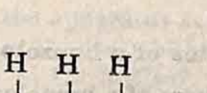
Alkenes and alkynes are hydrocarbons that contain double or triple bonds. An alkene (or olefin) contains a double bond between two carbon atoms. The simplest alkene is ethene, $C_2H_4$, which is commonly called ethylene.

Ethylene



$$\begin{array}{ccccccc} H & \dot{\times} & C & \dot{\times}\,\dot{\times} & C & \dot{\times} & H \\ & & \cdot\times & & \cdot\times & & \\ & & H & & H & & \end{array}$$

Electronic formula



$$\begin{array}{ccc} H & & H \\ & \rangle C=C\langle & \\ H & & H \end{array}$$

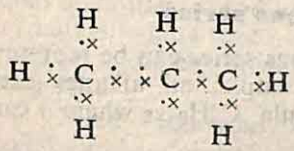
Structural formula

$H_2C=CH_2$

Condensed structural formula

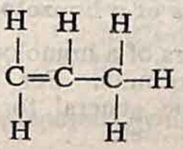
The second member of the alkene family is propene (or propylene), $C_3H_6$.

Propylene



$$\begin{array}{ccccccc} & & H & & H & & H \\ & & \cdot\times & & \cdot\times & & \cdot\times \\ H & \dot{\times} & C & \dot{\times}\,\dot{\times} & C & \dot{\times} & C\,\dot{\times}H \\ & & \cdot\times & & \cdot\times & & \cdot\times \\ & & H & & & & H \end{array}$$

Electronic formula



$$\begin{array}{ccccc} H & & H & & H \\ | & & | & & | \\ C & = & C & - & C-H \\ | & & & & | \\ H & & & & H \end{array}$$

Structural formula

$H_2C=CH-CH_3$

Condensed structural formula

There are other members in the alkene family, *e.g.* butene, $C_4H_8$ etc. They all have one double bond between two carbon atoms. The names of all alkenes end in "—ene".

Alkynes are hydrocarbons that contain a triple bond between two carbon atoms. The simplest alkyne is ethyne, $C_2H_2$, which is commonly called acetylene.

Ethyne

| | | |
|---|---|---|
| $H\dot{\times}C\dot{\times}\dot{\times}\dot{\times}C\dot{\times}H$ | $H-C\equiv C-H$ | $HC\equiv CH$ |
| Electronic formula | Structural formula | Condensed structural formula |

Other members of the alkyne family are 1-Propyne, ($C_3H_4$) 2-Butyne, ($C_4H_6$) etc. The names of all alkynes end in "—yne".

Alkenes and alkynes are called **unsaturated** hydrocarbons because they contain double or triple bonds. Their double or triple bonds allow other molecules to be added to the hydrocarbon chain through a reaction. For example, both an alkene and an alkyne can be converted to the corresponding alkane by an addition reaction with $H_2$. This reaction is called **hydrogenation** and is shown below :

$$\underset{\text{Ethyne}}{CH_2{=}CH_2} + \underset{\text{Hydrogen}}{H_2} \xrightarrow{\text{Ni/473K}} \underset{\text{Ethane}}{CH_3CH_3}$$

$$\underset{\text{Eythene}}{CH\equiv CH} + \underset{\text{Hydrogen}}{2H_2} \xrightarrow{\text{Ni}} \underset{\text{Ethane}}{CH_3CH_3}$$

The general formula of alkenes is $C_nH_{2n}$ ; the number of hydrogen atoms is twice the number of carbon atoms in the molecule. In case of alkyne family, the general formula is $C_nH_{2n-2}$. The formula shows that the number of hydrogen atoms is two less than twice the number of carbon atoms.

### 12.4. Homologous Series

It is observed from sections 12.2 and 12.3 that each hydrocarbon differs from the succeeding or the preceding one by a $-CH_2-$ unit and in molecular mass by 14. Any group of compounds in which the members differ in this manner is called a **homologous series.** The individual members of a homologous series are called **homologues.**

### 12.4.1. Characteristics of a homologous series

1. All the members of a homologous series can be represented by the same general formula. For example, all alkanes can be represented by the same general formula $C_nH_{2n+2}$ where $n$ can be given values 1, 2, 3, 4, ......etc.

2. Any two adjacent homologues differ by $-CH_2-$ unit. For example, propene ($C_3H_6$) and ethene ($C_2H_4$) differ by $-CH_2-$ unit.

3. The physical properties of the homologues show a gradual change with the increase in molecular masses. The m.p., b.p. and density usually increase with increase in molecular mass in a homologous series.

4. The homologues can be prepared by almost similar methods and have nearly similar chemical properties.

## 12.5. Ethane, $C_2H_6$

Ethane is the next higher homologue of methane. It occurs with methane in natural gas, coal gas, etc.

**Experiment 12.1.** To prepare ethane gas in the laboratory.

**Reaction.** Ethane gas is prepared in the laboratory by heating a mixture of sodium propionate and sodalime.

$$\underset{\text{Sodium propionate}}{CH_3CH_2COONa(s)} + NaOH(s) \xrightarrow[\text{CaO}]{\text{Heat}} \underset{\text{Ethane}}{CH_3\text{-}CH_3(g)} + \underset{\text{Sodium carbonate}}{Na_2CO_3(g)}$$

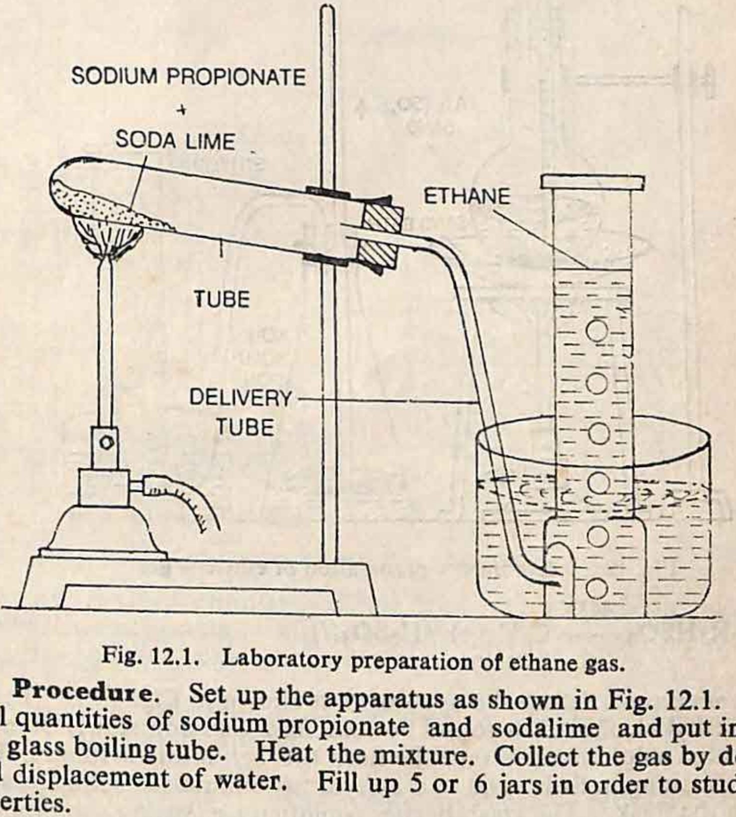


Fig. 12.1. Laboratory preparation of ethane gas.

**Procedure.** Set up the apparatus as shown in Fig. 12.1. Mix equal quantities of sodium propionate and sodalime and put into a hard glass boiling tube. Heat the mixture. Collect the gas by downward displacement of water. Fill up 5 or 6 jars in order to study its properties.

**Note.** Methane is prepared by heating a mixture of sodium acetate and sodalime.

## 12.6. Ethylene, $C_2H_4$

Ethylene is the first member of alkene series. It also occurs in natural gases obtained from oil fields.

**Experiment 12.2.** To prepare ethylene (ethene) gas in the laboratory.

**Reaction.** Ethylene or ethene is prepared in the laboratory by heating a mixture of ethyl alcohol (1 part) and concentrated sulphuric cid (2 parts). Sulphuric acid acts as a dehydrating agent. The rocess is then called acid catalyzed dehydration.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH(l)} + \underset{\text{(conc.)}}{H_2SO_4(l)} \longrightarrow \underset{\text{Ethylene hydrogen sulphate}}{C_2H_5HSO_4(l)} + H_2O(l)$$

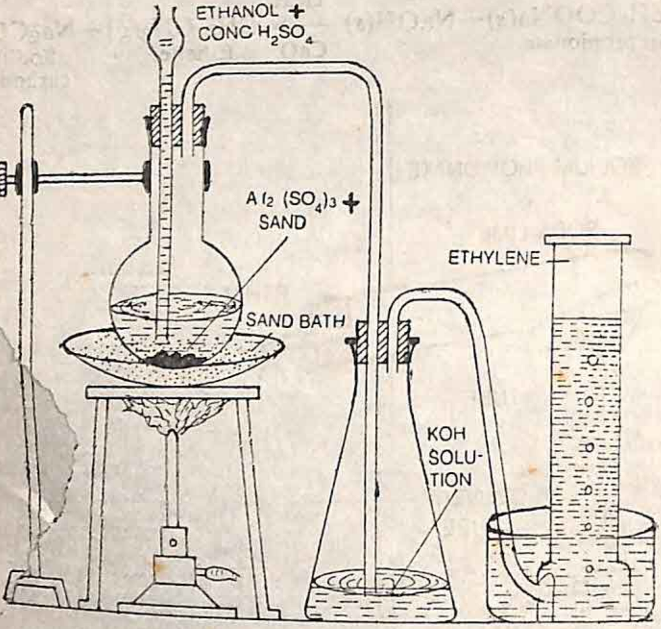


Fig. 12.2. Laboratory preparation of ethylene gas.

$$C_2H_5HSO_4 \xrightarrow{443K} \underset{\text{Ethylene}}{C_2H_4(g)} + H_2SO_4(l)$$

**Procedure.** Set up the apparatus as shown in Fig. 12.2. Take 25 mL ethyl alcohol in a round bottom flask and add slowly 50 mL concentrated sulphuric acid into the flask through a thistle funnel. To prevent frothing, a little sand and anhydrous aluminium sulphate are added to the flask. The wash bottle containing a strong solution of KOH is connected to the flask through a delivery tube. Heat the contents of the flask. Impurities like $CO_2$ and $SO_2$ are absorbed by KOH solution. Collect the gas by the downward displacement of water. Fill up 5 or 6 jars and study its properties.

## 12.7. Acetylene, $C_2H_2$

It is the first member of alkyne homologous series. It is also called ethyne. Traces of acetylene are present in coal gas.

**Experiment 12.3.** To prepare acetylene (ethyne) gas in the laboratory.

**Reaction.** In the laboratory acetylene is prepared by the action of water on calcium carbide.

$$\underset{\text{Calcium carbide}}{CaC_2(s)} + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + \underset{\text{Acetylene}}{C_2H_2(g)}$$

**Procedure.** Set up the apparatus as shown in Fig. 12.3. Take some small pieces of calcium carbide in a flat-bottom flask. Add water slowly to the flask through a thistle funnel until the lower end of the thistle funnel is under water. Acetylene gas is formed. Collect the gas in jars by the downward displacement of water.

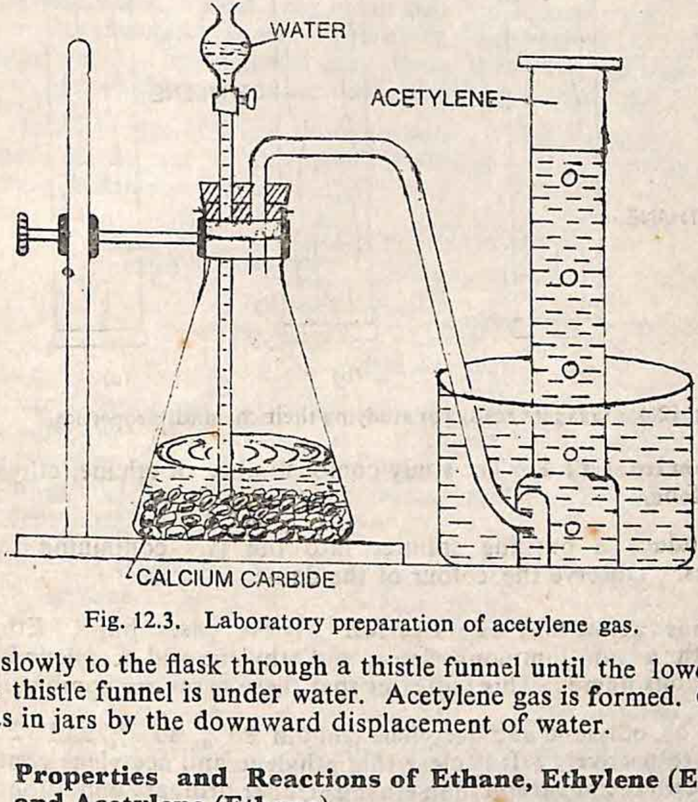


Fig. 12.3. Laboratory preparation of acetylene gas.

## 12.8. Properties and Reactions of Ethane, Ethylene (Ethene) and Acetylene (Ethyne)

**Physical properties.** These three gases ethane, ethylene and acetylene are colourless and odourless. These are insoluble in water but soluble in organic solvents like acetone, alcohol, ether, etc. Their m.p. and b.p. are as given below :

| *Gas* | *Melting point, K* | *Boiling point, K* |
|---|---|---|
| Ethane | 101 | 184 |
| Ethylene | 104 | 171 |
| Acetylene | 192 | 195 |

These gases are lighter than air.

**Chemical reactions.** To study chemical reactions of these three gases perform the following experiments. For each experiment take fresh samples of the gases in gas jars (Fig. 12.4).

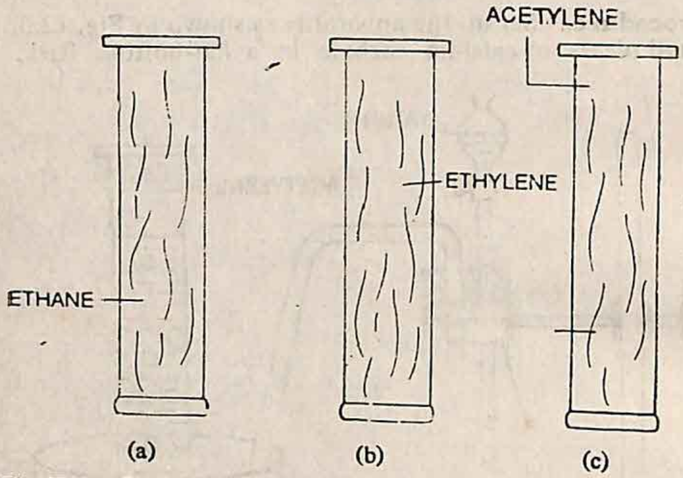


Fig. 12.4. Gas jars ready for studying their chemical properties.

**Experimet 12.4.** To study combustibility of ethane, ethylene and acetylene.

Introduce a burning splinter into the jars containing these three gases. Observe the colour of the flame.

**Observation and explanation.** These gases burn. Ethane burns with a non-luminous flame, and ethylene and acetylene burn with luminous flame. This indicates that these gases are combustible.

Ethane, ethylene and acetylene contain 80%, 85·7% and 92·3% of carbon respectively. It is clear that ethylene and acetylene contain higher percentage of carbon than ethane Under ordinary conditions of burning, all carbon particles are not oxidized which result luminous flame of ethylene and acetylene.

The three gases burn in air to produce carbon dioxide and water. These reactions are highly exothermic

$$2C_2H_6(g)+7O_2(g) \longrightarrow 4CO_2(g)+6H_2O(l)+3119{\cdot}6\ \text{kJ}$$

$$CH_2{=}CH_2(g)+3O_2(g) \longrightarrow 2CO_2(g)+2H_2O(l)+1411{\cdot}6\ \text{kJ}$$

$$2CH{\equiv}CH(g)+5O_2(g) \longrightarrow 4CO_2(g)+2H_2O(l)+2599{\cdot}2\ \text{kJ}$$

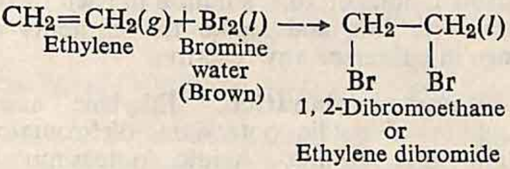
These three gases form highly explosive mixture with air. You should take all precautions while performing any experiment with any of these gases.

**Experiment 12.5**. To study the action of ethane, ethylene and acetylene with bromine water.

Take bromine water in a test tube. Add about 2 mL of it in each of the three gas jars. Cover these gas jars with lids and shake the contents well. Observe any change in colour of bromine water.

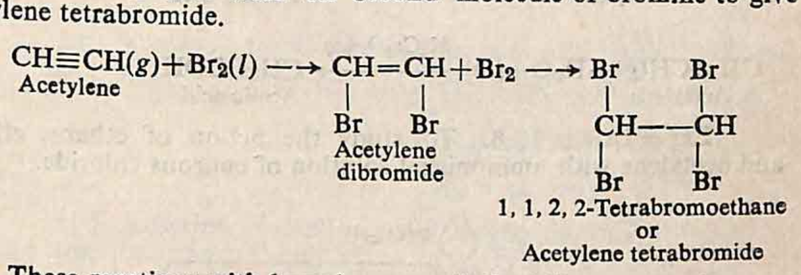
**Observation and explanation**. Ethylene and acetylene decolourize bromine water. There was no action of ethane on bromine water. This indicates that ethane is a saturated hydrocarbon, and ethylene and acetylene are unsaturated hydrocarbons.

Ethylene decolourizes bromine water. This is because bromine is used up by the double bond of ethene and a colourless product ethylene bromide is formed.



$$\underset{\text{Ethylene}}{CH_2{=}CH_2(g)}+\underset{\substack{\text{Bromine}\\ \text{water}\\ \text{(Brown)}}}{Br_2(l)} \longrightarrow \underset{\substack{\text{1, 2-Dibromoethane}\\ \text{or}\\ \text{Ethylene dibromide}}}{\underset{\substack{|\\ Br}}{CH_2}-\underset{\substack{|\\ Br}}{CH_2}(l)}$$

Acetylene contains one triple bond. So it is more unsaturated than ethylene. It adds on two molecules of bromine. First one molecule adds to give acetylene dibromide. Acetylene dibromide is still unsaturated and adds on second molecule of bromine to give acetylene tetrabromide.



$$\underset{\text{Acetylene}}{CH{\equiv}CH(g)}+Br_2(l) \longrightarrow \underset{\substack{\text{Acetylene}\\ \text{dibromide}}}{\underset{\substack{|\\ Br}}{CH}{=}\underset{\substack{|\\ Br}}{CH}}+Br_2 \longrightarrow \underset{\substack{\text{1, 1, 2, 2-Tetrabromoethane}\\ \text{or}\\ \text{Acetylene tetrabromide}}}{\overset{\substack{Br\\ |}}{\underset{\substack{|\\ Br}}{CH}}-\overset{\substack{Br\\ |}}{\underset{\substack{|\\ Br}}{CH}}}$$

These reactions with bromine are called **addition reactions.**

**Experiment 12.6**. To study the action of ethane, ethylene and acetylene with alkaline potassium permanganate.

Prepare 10 mL of 1% aqueous solution of potassium permanganate in a test tube. Make it alkaline by dissolving about 1 g of sodium carbonate in it. Now add 1 mL of this solution in each of the three gas jars containing these gases. Cover the gas jars with lids and shake the contents well. Observe any change in pink colour of potassium permanganate or any other reaction.

**Observation and explanation**. Ethylene and acetylene decolourize alkaline potassium permanganate solution (Baeyer's reagent). There is no decolourization with ethane. This indicates that ethylene and acetylene are unsaturated ; ethane is a saturated hydrocarbon. Ethylene is oxidized to ethylene glycol and acetylene is oxidized to oxalic acid.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2(g)}+H_2O+[O] \xrightarrow{KMnO_4(aq)} \underset{\text{Ethylene glycol}}{CH_2OH{-}CH_2OH}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH(g)}+4[O] \xrightarrow{KMnO_4(aq)} \underset{\text{Oxalic acid}}{HOOC{-}COOH}$$

Bromine water and alkaline potassuim permanganate are reagents used to test for unsaturation in an organic compound.

**Experiment 12.7.** To study the action of ethane, ethylene and acetylene with acidic potassium dichromate.

Prepare 10 mL of 1% aqueous solution of potassium dichromate in a test tube. Make it acidic by adding 1 or 2 drops of concentrated sulphuric acid. Add 1 mL of this solution in each of the three gas jars. Cover them with lids and shake the contents of the jars. Observe any change in colour or any reaction.

**Observation and explanation.** Ethylene and acetylene change orange colour of acidic potassium dichromate to green. There is no action with ethane. Acidic potassinm dichromate oxidizes ethylene to formic acid and acetylene to acetic acid.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2(g)}+4[O] \xrightarrow{K_2Cr_2O_7(aq)} \underset{\text{Formic acid}}{2HCOOH}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH(g)}+H_2O+[O] \xrightarrow{K_2Cr_2O_7(aq)} \underset{\text{Acetic acid}}{CH_3COOH}$$

**Experiment 12.8.** To study the action of ethane, ethylene and acetylene with ammoniacal solution of cuprous chloride.

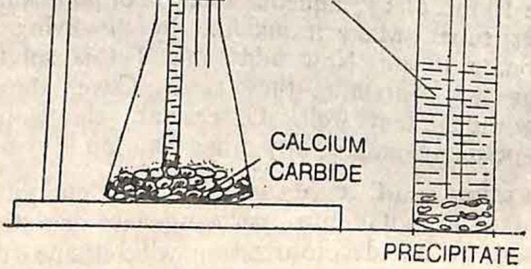


Fig. 12.5. Demonstration of the action of ammoniacal cuprous chloride solution on a acetylene gas.

Prepare 10 mL ammoniacal solution of cuprous chloride by dissolving 0·5 g of cuprous chloride in dilute ammonium hydroxide solution. Take 2 mL of this solution in a test tube and pass ethane gas through it. Observe any change in colour or formation of a precipitate. Repeat this with other two gases taking fresh samples of ammoniacal cuprous chloride in each case. Figure 12.5. shows action of acetylene with ammoniacal solution of cuprous chloride.

**Observation and explanation.** Acetylene gives reddish brown precipitate when bubbled through ammoniacal solution of cuprous chloride. No reaction is observed with ethane and ethylene.

Hydrogen atoms of acetylene are replaced by copper forming dicopper acetylide.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{[Cu(NH_3)_2]Cl} \underset{\substack{\text{Copper}\\ \text{acetytide}}}{CH\equiv CCu(s)} \xrightarrow{[Cu(NH_3)_2]Cl} \underset{\substack{\text{Dicopper acetylide}\\ \text{(Reddish brown ppt.)}}}{CuC\equiv CCu(s)}$$

**Tests for Acidic Nature of Acetylene**

(*i*) Acetylene when passed through ammoniacal silver nitrate solution gives a white precipitate of disilver acetylide.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{[Ag(NH_3)_2]NO_3} \underset{\substack{\text{Silver}\\ \text{acetylide}}}{CH\equiv CAg(s)} \xrightarrow{[Ag(NH_3)_2]NO_3} \underset{\substack{\text{Disilver}\\ \text{acetylide}\\ \text{(White ppt.)}}}{AgC\equiv CAg(s)}$$

(*ii*) Acetylene reacts with sodium amide in liquid ammonia :

$$HC\equiv CH + NaNH_2(NH_3) \longrightarrow HC\equiv CNa(NH_2) + NH_3 \rightarrow$$

$$\longrightarrow \underset{\substack{\text{Sodium}\\ \text{dicarbide}}}{NaC\equiv CNa} + NH_3$$

(*ii*) Reaction of ammoniacal cuprous chloride with acetylene as discussed in experiment 12.8.

**Explanation**

These are substitution reactions. Here acidic H has been replaced by some metals. A terminal triple bond reacts with certain bases, the terminal hydrogen atom being replaced by a metal ion. These bases are : sodium amide in liquid ammonia, Cu (I) ion in aqueous ammoniacal solution, and Ag (I) ions in aqueous ammoniacal solution.

The reason for the acidity of the hydrogen atom attached to a terminal triple bond is that the negative charge on the anion $RC\equiv C^-$, can be delocalized by interaction with the cloud of $\pi$ electrons in the $C\equiv C$ bond. This reduces the charge on the terminal carbon atom and reduces its attraction for a proton.

Table 12.1 gives the summary of all the experiments performed and their results.

**Table 12.1. Specimen record of properties of ethane, ethylene and acetylene**

| *S. N.* | *Experiment* | *Observation* | *Inference* |
|---|---|---|---|
| 1. | Observe the colour of gases in the jars | Colourless | The three gases are colourless |
| 2. | Note odour of gases | Odourless | The three gases are odourless |
| 3. | Solubility in water (gases are collected by downward displacement of water) | Insoluble | The three gases are insoluble in water |
| 4. | Combustion :<br>Introduce a buring splinter in the gas jars | The three gases burn ; Ethane burns with a non-luminous flame, and ethylene and acetylene burn with a luminous flame | All the three gases are combustible |
| 5. | Add bromine water to each of the three gas jars or bubble gas through bromine water | There is a decolourization with ethylene and acetylene but no reaction with ethane | Ethylene and acetylene are unsaturated hydrocarbons, and ethane is a saturated hydrocarbon. |
| 6. | Add alkaline $KMnO_4$ solution to each of the three gas jars or bubble gas through alkaline $KMnO_4$ solution. | Pink colour is decolourized with ethylene and acetylene. No action with ethane | Same as above |
| 7. | Add acidic $K_2Cr_2O_7$ solution to each of the three gas jars or bubble through acidic $K_2Cr_2O_7$ solution. | Orange colour is changed to green with ethylene and acetylene. No action with ethane | Acidic $K_2Cr_2O_7$ oxidizes ethylene and acetylene |
| 8. | Pass ethane, ethylene and acetylene through ammoniacal cuprous chloride solution taken in three test tubes. | Only acetylene gives reddish brown precipitate | Copper replaces hydrogen atoms in acetylene giving dicopper acetylide ($Cu_2C_2$). Acetylene is acidic in nature. |

## 12.9. Tests for Ethane, Ethylene and Acetylene

With samples of these three gases, perform the tests listed in Table 12.2. You would be able to distinguish between ethane, ethylene and acethylene.

**Table 12.2. Tests for ethane, ethylene and acetylene**

| *S.N.* | *Tests* | *Ethane* | *Ethylene (ethene)* | *Acetylene (ethyne)* |
|---|---|---|---|---|
| 1. | Action of bromine water | No reaction | Brown colour turns colourless | Brown colour turns colourless. |
| 2. | Action of alkaline $KMnO_4$ solution | No reaction | Pink colour turns colourless | Pink colour turns colourless. |
| 3. | Action of ammoniacal $Cu_2Cl_2$ solution | No reaction | No reaction | Reddish brown precipitate. |

## ORAL QUESTIONS AND ANSWERS

**Q. 12.1.** What is the difference in the molecular formula of any two adjacent members of a homologus series of hydrocarbons.

(*i*) in terms of molecular mass.

(*ii*) in terms of number and kind of atoms in their molecules.

**Ans.** (*i*) 14 (*ii*) $-CH_2-$

**Q. 12.2.** Select the hydrocarbons from the following which are members of the same homologous series. Also give the name of each homologous series representing the hydrocarbons.

$CH_4$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_4H_{10}$, $C_3H_4$, $C_3H_6$

**Ans.** Homologous series :

Alkane $CH_4$, $C_2H_6$, $C_4H_{10}$

Alkene $C_2H_4$, $C_3H_6$

Alkyne $C_2H_2$, $C_3H_4$

**Q. 12.3.** Which hydrocarbon decolourizes bromine water and gives white precipitate with ammoniacal solution of silver nitrate ?

**Ans.** Acetylene

**Q. 12.4.** Which of the following compounds will give an addition reaction ?

$C_2H_6$, $C_3H_8$, $C_2H_4$, $C_3H_4$, $C_2H_2$, $C_6H_{14}$

**Ans.** $C_2H_4$, $C_3H_4$, $C_2H_2$.

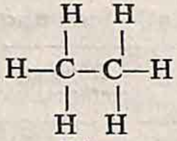
**Q. 12.5.** Give two examples of each of the following :

(*i*) Saturated hydrocarbons

(*ii*) Unsaturated hydrocarbons

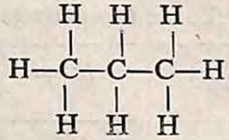
Write names and structural formulae of the examples you give.

**Ans.** (*i*)



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

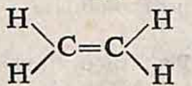
Ethane



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

Propane

(*ii*)



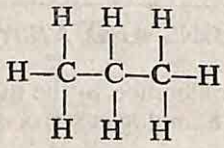
Ethylene

$H-C \equiv C-H$

Acetylene

**Q. 12.6.** Write the structural formula of a saturated hydrocarbon containing 3 carbon atoms in its molecule.

**Ans.**



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

Propane

**Q. 12.7.** What is the general name given to all the compounds containing only carbon and hydrogen ?

**Ans.** Hydrocarbons.

**Q. 12.8.** The general molecular formula of alkanes is $C_nH_{2n+2}$. What will be the general molecular formula for

(*i*) alkenes, and (*ii*) alkynes ?

**Ans.** (*i*) $C_nH_{2n}$ (*ii*) $C_nH_{2n-2}$

**Q. 12.9.** Write the molecular formulae of :

(*i*) first four members of the homologous series of alkanes.

(*ii*) first two members of the homologous series of alkenes.

(*iii*) first two members of the homologous series of alkynes.

**Ans.** (*i*) $CH_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$

(*ii*) $C_2H_4$, $C_3H_6$

(*iii*) $C_2H_2$, $C_3H_4$

**Q. 12.10.** Complete the following reactions :

(*i*) $CH_2{=}CH_2+Br_2(aq) \longrightarrow$

(*ii*) $CH{\equiv}CH+Br_2\,(aq) \longrightarrow$

**Ans.** (*i*) $\rightarrow CH_2Br{-}CH_2Br$

1, 2-Dibromoethane

or Ethylene dibromide

(*ii*) $\rightarrow CHBr{=}CHBr$
1, 2-Dibromoethene
or Acetylene dibromide

$\longrightarrow CHBr_2{-}CHBr_2$
Acetylene tetrabromide

**Q. 12.11.** Why does ethylene decolourize bromine water, while ethane does not do so ?

**Ans.** Ethylene is an unsaturated hydrocarbon and forms addition compound with bromine water. Ethane is a saturated hydrocarbon and does not react with bromine water.

**Q. 12.12.** Give one example of addition reaction of chlorine.

**Ans.** $\underset{\text{Ethylene}}{CH_2{=}CH_2} + Cl_2 \longrightarrow \underset{\text{Ethylene dichloride}}{CH_2ClCH_2Cl}$

**Q. 12.13.** Name the products obtained by the combustion of saturated and unsaturated hydrocarbons.

**Ans.** $CO_2$ and $H_2O$

**Q. 12.14.** Ethane burns in oxygen to form carbon dioxide and water. Write balanced chemical equation for this reaction.

**Ans.** $2CH_3CH_3 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

**Q. 12.15.** What do you understand by unsaturation ? How will you test unsaturation in an organic compound ?

**Ans.** Organic compounds in which there is at least one double or triple bond in carbon chain are called unsaturated compounds. In such compounds carbon atoms combine with another through two or three pairs of electrons. An unsaturated compound is reactive particularly for addition reactions. Such a property of unsaturated compounds is called unsaturation.

Bromine water is instantly decolourized by unsaturated compounds due to addition reactions. Now, if on adding a few drops of aqueous bromine to the organic compound, the brown colour of bromine is discharged, then the compound is unsaturated.

□ □

# UNIT 13

# Organic Liquids—Their Separation and Purification

## 13.1. Introduction

A pure substance is defined as any kind of matter of which all samples have identical composition and identical properties. For example, all samples of methyl alcohol contain exactly the same proportion of carbon, hydrogen and oxygen, regardless of the sources of samples. All samples have the same boiling points. Pure substances may be elements or compounds : when elements or compounds are mixed, a mixture is formed. The various constituents of a mixture have different physical properties. This difference in their physical properties is utilized to separate them from a mixture. The constituents of a mixture can be separated by physical methods like sedimentation and decantation, filtration, evaporation, sublimation, distillation, crystallization, magnet, separating funnel, etc.

## 13.2. Distillation

**Distillation** is a process where a liquid on heating changes into vapours and then vapours on cooling convert into liquid (Fig. 13.1). This method is employed to separate a mixture when both components are liquids or one is a soluble solid and the other is a liquid. This method is quite useful in purifying liquids and is based on differences in boiling points. From a mixture containing ether (b.p. 308K) and other liquids (boiling points above 373K), the former is separated by distillation. In case the liquid to be purified is high boiling or decomposes below its boiling point, the distillation is carried under reduced pressure (Fig. 13.2). When the boiling points of the liquids are close to each other as in the case of acetone (b.p. 333K) and methyl alcohol (b p. 338K) they can be separated by fractional distillation (Fig. 13.3) using a fractionating column.

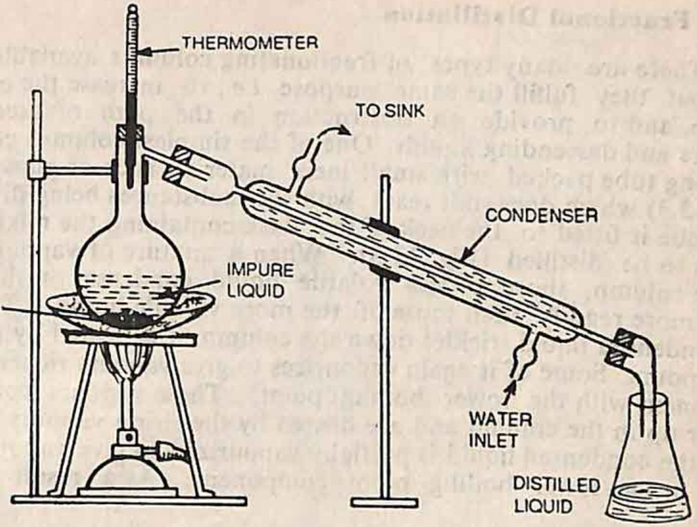


Fig. 13.1. An assembly for distillation

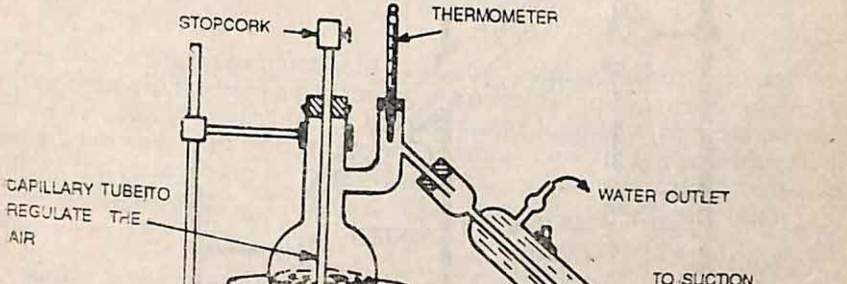


Fig. 13.2. An assembly for distillation under reduced pressure

## 13.3. Fractional Distillation

There are many types of fractionating columns available (Fig. 13.4) but they fulfill the same purpose *i.e.*, to increase the cooling surface and to provide an obstruction in the path of ascending vapours and descending liquids. One of the simplest columns consists of a long tube packed with small inert materials such as glass beads (Fig. 13.3) which does not react with the substances being distilled. This tube is fitted to the neck of the flask containing the mixture of liquids to be distilled (Fig. 13.3). When a mixture of vapours rises up the column, those of less volatile liquid condense on the glass beads more readily than those of the more volatile liquid. Then as the condensed liquid trickles down the column, it is heated by the rising vapours. Some of it again vapourizes to give vapours richer in the component with the lower boiling point. These vapours condense further up in the column and are heated by the rising vapours And again the condensed liquid is partially vapourized to give vapours still richer in the lower boiling point component. As a result of the

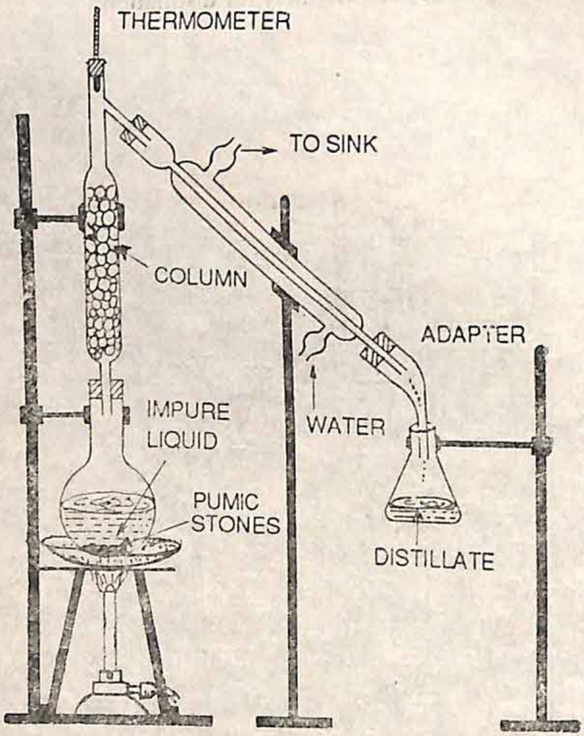


Fig. 13.3. An assembly for fractional distillation

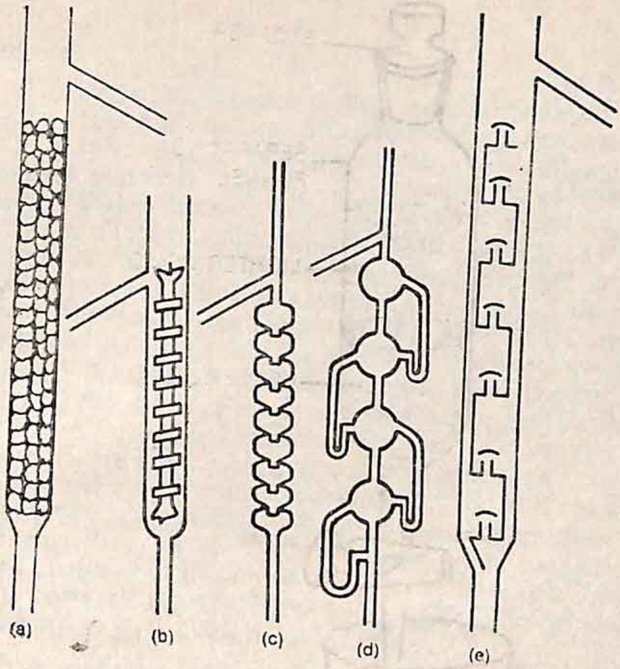


Fig. 13.4. Fractionating columns

many vapourizations (evaporation) and condensations, the vapours ascending the column become progressively richer in the more volatile liquid *i.e.*, richer in the lower boiling point liquid. The vapours emerging from the top of a column condense to a liquid which is essentially the pure lower boiling point component, and this is then collected in the receiver. This process is known as fractional distillation.

## 13.4. Separating funnel

A mixture of two immiscible liquids can be separated by using a separating funnel. When the mixture of two immiscible liquids is taken in a separating funnel (Fig. 13.5) the heavier liquid forms the lower layer and the lighter layer forms the upper layer. On opening the tap, the lower layer comes down first, followed by the upper layer. A mixture of benzene and water can be separated by this method.

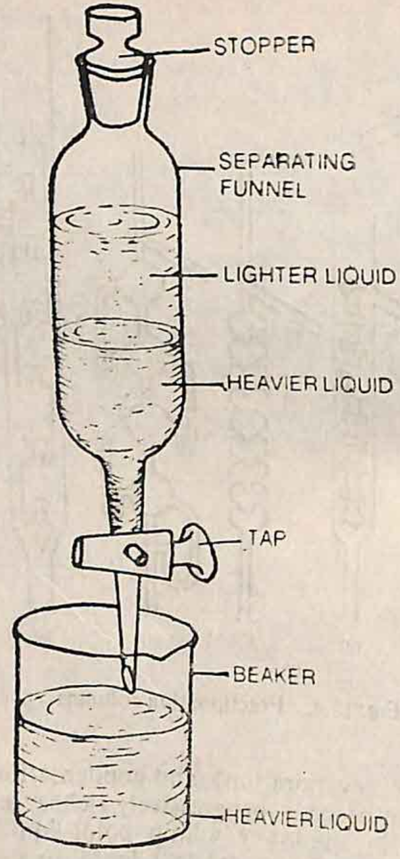


Fig. 13.5. Separating funnel

## 13.5. Experiments

**Experiment 13.1.** To separate a mixture of two liquids having different boiling points.

**Apparatus.** Round bottom flask, burner, tripod, iron stand, clamps, thermometer, fractionating column, air condenser, water condenser, adaptor, conical flasks, beakers etc.

**Chmicals.** A mixture of liquids (miscible)

**Theory.** The separation of the components of a mixture depends upon the boiling points of the constituents of the mixture. In case the difference in the boiling points of the liquids are large, a technique of simple distillation is used. When the boiling points of the liquids are close to each other, fractional distillation is used.

**Procedure**

(*a*) **Simple Distillation.** Set up the apparatus as shown in Fig. 13.1. Take the mixture of the liquids (say water b.p. 100°C and glycol b.p 179°C, whose boiling points are very different) in a round bottom flask and start heating. On heating for some time, the contents of the flask will start boiling and vapours will start forming in plenty. The vapours entering the condenser will be richer in water than in glycol. So the resulting liquid (distillate) will contain a higher proportion of water and lower proportion of glycol than the original mixture. The liquid remaining in the flask will contain a higher proportion of glycol. Collect the sample of distillate obtained at 100°C in a beaker. When the whole of water will be converted into vapours, temperature will start rising. At this stage, collect the sample of distillate in a separate beaker. After some time you will observe that temperature start rising fast. Now replace the water condenser by air condenser. When the thermometer shows a reading of 179°C, start collecting the distillate. Redistillation of the first distillate will further enrich it in the lower boiling point component and by repeated distillations a sample of pure water will be obtained. Treat the last distillate on the same lines. After repeated distillations a pure sample of glycol will be obtained.

**Precautions.** 1. In order to ensure uniform heating, add same pumic stones into the flask.

2. For liquids having b.p. $< 100$°C use water condenser.

3. For liquids having b.p.$>100$°C or more use air condenser.

(*b*) **Fractional Distillation.** Set up the apparatus as shown in Fig. 13.3. Take the mixture of two liquids whose boiling points are close to each other (*e.g.*, acetone, b.p. 333K and methyl alcohol b.p 338K). Now start heating the mixture. After heating the mixture for some time vapours will start rising. The ascending vapours will soon start condensing. The condensed vapours will contain more of methyl alcohol, a less volatile liquid. Condensed liquid will further come across the rising vapours and thus some of it will again vapourize. As a result of continuous vapourizations and condensations, the vapours moving up the column will become progressively richer in the more volatile liquid *i.e.* acetone. At the top of the column the vapours will be of acetone only. Collect them in the receiver which will condense after they pass through the water condenser. After some time you will observe that the thermometer continues to show the same reading until acetone is completely separated. When the temperature starts rising, remove this receiver and put another one. At this stage, the distillate will be a mixture of acetone and methyl alcohol. When again the temperature is stabilized replace this receiver. Now the vapours emerging from the top of column will condense to a liquid which is essentially the pure methyl alcohol, a higher-boiling point component.

**Experiment 13.2.** To separate a mixture of two liquids immiscible with each other.

**Apparatus.** Tripod, conical flasks, beakers, separating funnel.

**Chemicals.** A mixture of liquids.

**Theory.** The separation of the components of a mixture depends upon the density of the constituents of the mixture.

**Procedure.** Take the mixture (water and benzene) in the separating funnel. Soon the heavier liquid *i.e.* benzene will form the lower layer. Now open the tap and the lower layer will start coming down. Collect the liquid in a receiver. Now put another receiver. This receiver will contain a mixture of the two liquids. When the upper layer starts coming down, replace the receiver and collect it. Thus the separation of two immiscible liquids will be achieved.

## ORAL QUESTIONS AND ANSWERS

**Q. 13.1.** What is condensation ?

**Ans.** It is a process in which a substance changes from the gaseous form (vapour) to the liquid form.

**Q. 13.2.** What is distillation ?

**Ans.** It is a process of purifying liquids in which they are changed into vapours and then condensed back to the liquid form.

□ □

# UNIT 14

# Displacement Reactions

## 14.1. Introduction

All the reactions you have come across involve the loss and gain of electrons. When a metal reacts, the lattice loses electrons, forming positive ions. The electrochemical series based on electrode potential tells you how easily this process takes place when metals react with water, acids or solutions of other metal salts. These electrons lost from the metal atoms may be consumed by :

hydrogen atoms in water on acids.

the ions of a less reactive metal, or

the atoms of a non-metal.

When non-metals react, their atoms accept electrons, and thereby become negative ions. These electrons, gained or accepted by the non-metal atoms have been lost (or supplied) from :

metals atoms or

less reactive non-metal ions.

So all these reactions involve the transfer of electrons from the atoms or ions of one element to the atoms or ions of another element when one species loses electrons another gains them.

Oxidation is the loss of electrons by atoms, ions or molecules and reduction is the gain of electrons by atoms, ions or molecules. Since there cannot be a net loss or gain of electrons in a chemical reaction—only a transfer among substances-oxidation and reduction must always occur as concurrent reactions in equivalent amounts. Such coupled reactions are called **redox reactions**. A large number of redox reactions are possible which arise from various combinations of pairs of oxidants and reductants.

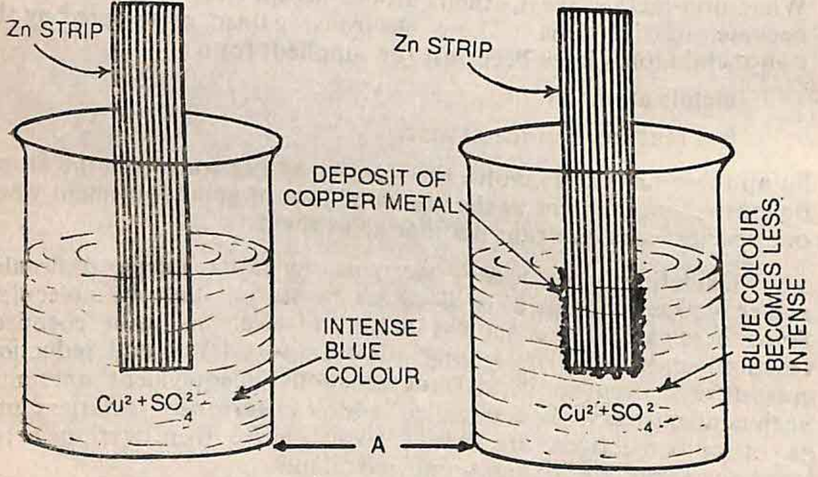
Any substance that promotes the loss of electrons because of its tendency to gain them is called an oxidizing agent. Any substance that readily gives up its electrons is called a reducing agent, Thus, in a reaction oxidizing agents get reduced and reducing agents are oxidized. Under the circumstances, the oxidation state of any substance may be used to predict the tendency of a material to act as an oxidizing agent or a reducing agent. A knowledge of common oxidizing agents and reducing agents can help us design reactions in which selected substances can be oxidized or reduced.

## 14.2. Displacement Reaction

A displacement reaction is a reaction in which an atom, or a group of atoms, present in a molecule is displaced by another atom.

Consider the reaction between zinc metal and copper (II) sulphate solution and also between copper metal and silver nitrate solution. The zinc strip is immersed in a solution of copper sulphate contained in a beaker A (Fig. 14.1) and the copper strip is placed in a solution of silver nitrate contained in a beaker B (Fig. 14.2). We observe some reactions in the beakers and allow to proceed for some time say 10 minutes. After 10 minutes, we observe some metallic deposit on the two strips. Why does this change take place on the metallic surface ? This is an oxidation-reduction reaction. The reaction of zinc metal with copper sulphate can be considered in two half-reactions.

Oxidation : $Zn(s) \longrightarrow Zn^{2+}(aq)+2e^{-}$
Reduction : $Cu^{2}(aq)+2e^{-} \longrightarrow Cu(s)$
Net reaction : $Zn(s)+Cu^{2+}(aq) \longrightarrow Cu(s)+Zn^{2+}(aq)$



$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

Fig. 14.1. Behaviour of zinc towards aqueous solution of copper sulphate ; zinc metal displaces copper from copper sulphate

Zinc loses electrons and is, therefore, oxidized and $Cu^{2+}$ ion gains electrons and is, therefore, reduced.

$$\overset{-2e^-\ \text{Oxidation}}{Zn(s)+Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq)}+Cu(s)$$
$$\underset{+2e^-\ \text{Reduction}}{Zn(s)+Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq)+Cu(s)}$$

In this reaction $Cu^{2+}$ ions are displaced from the solution by zinc ions and $Cu^{2+}$ ions after accepting electrons get deposited on the zinc strip. Similarly the displacement of silver from silver nitrate in the presence of copper strip can be portrayed.

$$\overset{-2e^-\text{—(Oxidation)}}{Cu(s)+2Ag^+(aq) \longrightarrow Cu^{2+}(aq)}+2Ag(s)$$
$$\underset{+2e^+\text{—Reduction}}{Cu(s)+2Ag^+(aq) \longrightarrow Cu^{2+}(aq)+2Ag(s)}$$

This is an oxidation-reduction which can be considered in two half reactions

Oxidation : $Cu(s) \longrightarrow Cu^{2+}(aq)+2e^-$

Reduction : $Ag^+(aq)+e^- \longrightarrow Ag(s)$

Net reaction : $Cu(s)+2Ag^+(aq) \longrightarrow Cu^{2+}(aq)+2Ag(s)$

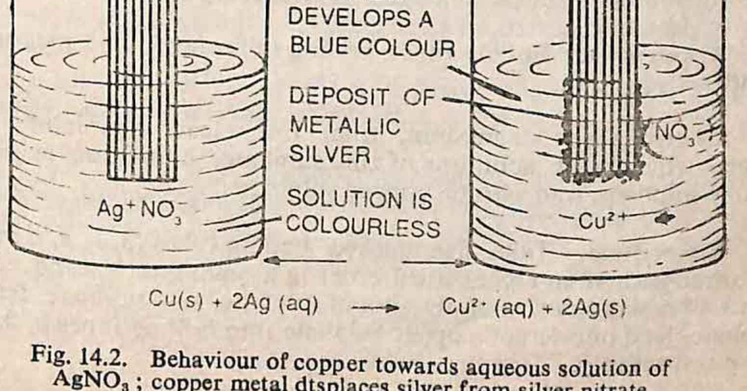

Cu
Cu
SOLUTION DEVELOPS A BLUE COLOUR
DEPOSIT OF METALLIC SILVER
SOLUTION IS COLOURLESS
Ag⁺ NO₃⁻
NO₃⁻
Cu²⁺
Cu(s) + 2Ag (aq) → Cu²⁺ (aq) + 2Ag(s)

Fig. 14.2. Behaviour of copper towards aqueous solution of $AgNO_3$ ; copper metal dtsplaces silver from silver nitrate

On the other hand if a copper plate is immersed in a solution of $Zn(NO_3)_2$ (or $ZnSO_4$) no reaction takes place (Fig. 14.3).

Why does copper behave differently towards $Ag^+$ and $Zn^{2+}$ ions ? The answer to this lies with the relative tendency of accepting elecrons by $Ag^+$ and $Zn^{2+}$ ions. Obviously $Ag^+$ ions have a greater tendency to gain electrons (a greater tendency toward reduction) than $Zn^{2+}$ ions. Thus, a fair knowledge of relative oxidation and reduction tendencies is essential in understanding the direction of spontaneous **change in redox reactions (or displacement reactions).**

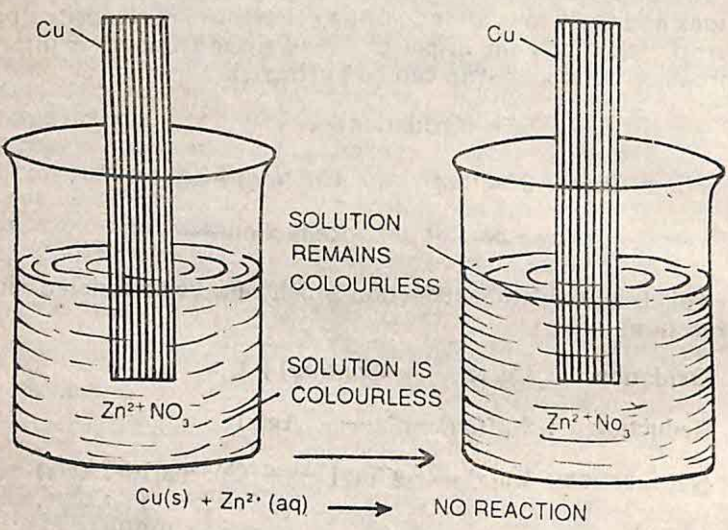


Fig. 14.3. Behaviour of copper towards aqueous solution of $Zn(NO_3)_2$ copper metal does not displace zinc from zinc nitrate.

## 14.3. Experiments

**Experiment 14.1**. To study the interactions of some metals with salt solutions and arranging them according to their activity.

**Apparatus.** Boiling tubes, boiling tube stand, and measuring cylinder.

**Chemicals.** Magnesium, zinc, iron, lead aluminium and copper strips, molar solutions of zinc sulphate, aluminium sulphate, ferrous sulphate, lead nitrate, copper sulphate.

**Procedure**. Take five marked boiling tubes (*a*, *b*, *c*, *d* and *e*) and arrange them in alphabetical order in a boiling tube stand. Pour 50 mL of molar solution of aluminium sulphate, zinc sulphate, ferrous sulphate, lead nitrate and copper sulphate into boiling tubes *a*, *b*, *c*, *d* and *e* respectively.

Dip pure magnesium strips in all the five boiling tubes for about 1/2 hour. Observe the deposition of metals on the strips. Record the observations in the tabular form. Repeat the experiment with different metals and record the observations in the tabular form.

**Observations**

| *Pure metal* | *Added to solutions of the metal salts* | | | | |
|---|---|---|---|---|---|
| | $Al_2(SO_4)_3$ | $ZnSO_4$ | $FeSO_4$ | $Pb(NO_3)_2$ | $CuSO_4$ |
| Mg | Displacement | Displacement | Displacement | Displacement | Displacement |
| Al | No reaction | Displacement | Displacement | Displacement | Displacement |
| Zn | No reaction | No reaction | Displacement | Displacement | Displacement |
| Fe | No reaction | No reaction | No reaction | Displacement | Displacement |
| Pb | No reaction | No reaction | No reaction | No reaction | Displacement |

**Conclusion**. In these experiments, you will find that displacement reactions take place. Metal from the strip dissolves. At the same time metal displaces the metal from the solution of their salts. From the table one can infer that aluminium is quite a reactive metal, displacing four other metals from their salt solutions.

The table also shows that a solution of $Al_2(SO_4)_3$ is fairly unreactive ; only magnesium can displace aluminium from it. The results for lead and its salt are the reverse of this. Lead metal is quite unreactive, displacing only copper from its salt solution. However, a solution of lead nitrate is quite a reactive one ; four metals can displace lead from it.

**The more reactive a metal is, the more unreactive are its salts in solution. Its ions will be difficult to displace.**

**An unreactive metal will have reactive ions which are easy to displace from solution.**

On the basis of experimental observations, the metals and their ions can be arranged in order of their activity.

**The reactivity series for metals and their ions**

| *Metals* | | *Metal ions* | |
|---|---|---|---|
| Magnesium | ↑ Increasingly reactive | $Mg^{2+}(aq)$ | Increasingly reactive ↓ |
| Aluminium | | $Al^{3+}(aq)$ | |
| Zinc | | $Zn^{2+}(aq)$ | |
| Iron | | $Fe^{2+}(aq)$ | |
| Tin | | $Sn^{2+}(aq)$ | |
| Lead | | $Pb^{2+}(aq)$ | |
| Copper | | $Cu^{2+}(aq)$ | |

The table shows that the metals follow the order in which they appear in the electrochemical series (based on the electrode potential).

A simple rule, that works for all the experiments, can be discovered from the results.

Any metal in the electrochemical series can displace (reduce) a metal lower in the series from solutions of its salts/compounds.

## ORAL QUESTIONS AND ANSWERS

**Q. 14.1.** State which of the followings best describes the type or types of reaction that takes place in the experiment 14.1.

(*a*) Precipitation, (*b*) Oxidation, (*c*) Reduction, (*d*) Reduction/oxidation (*e*) Decomposition

**Ans.** (*d*) Reduction/oxidation

**Q. 14.2.** State which of the followings represents the order of the metals in the electrochemical series.

(*a*) Copper, tin, iron, zinc
(*b*) Zinc, iron, tin, copper
(*c*) Zinc, tin, copper, iron.
(*d*) Iron, copper, tin, zinc.

**Ans.** (*b*) Zinc, iron, tin, copper.

**Q. 14.3.** Can a displacement reaction be considered a redox reaction.

**Ans.** Yes, See Section 14.2.

**Q. 14.4.** Can a reaction between a metal and an acid or water be termed a displacement reaction ?

**Ans.** Yes. Because the metal displaces hydrogen etc. from the acid solution or water.

## UNIT 15

# The Concept of pH and Determination of pH of Some Solutions

### 15.1. Introduction

Solutions of acids and bases in water may have $H_3O^+$ and $OH^-$ concentrations that vary over a wide range, that is, from greater than 1 mol $L^{-1}$ down to $10^{-14}$ mol $L^{-1}$ or lower. Acidic solutions have $[H_3O^+]$ greater than $10^{-7}$ mol $L^{-1}$ and $[OH^-]$ less than $10^{-7}$ mol $L^{-1}$ at 298K. Basic (alkaline) solutions have $[OH^-]$ greater than than $10^{-7}$ mol $L^{-1}$ and $[H_3O^+]$ less than $10^{-7}$ mol $L^{-1}$ at 298K. A neutral solution such as pure water has $[H_3O^+]=[OH^-]=10^{-7}$ mol $L^{-1}$

We have seen that it is possible to describe acidity or basicity of a solution by specifying the concentration of $H_3O^+$ ions. A Danish biochemist, Peter Sorenson, in 1909, proposed a new system, to avoid the use of negative powers of 10, known as pH scale. He defined pH as follows :

The pH of a solution is the negative logarithm to the base of 10 of the hydrogen ion concentration $[H_3O^+]$.

Thus, $pH=-\log_{10}[H_3O^+]=\log_{10}\frac{1}{[H_3O^+]}$

The small p in pH is derived from the German word 'potenz' meaning power. Thus, pH means power of hydrogen ion.

In the same way, one can define the pOH as follows :

$$pOH=-\log[OH^-]$$

Water is only slightly ionized,

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The product of the concentrations of hydrogen ions and hydroxide ions is equal to $1{\cdot}0\times10^{-14}$ mol$^2$ $L^{-2}$ at 298K. This product is called the ionic product for water, Kw.

$$[H_3O^+][OH^-]=Kw=1{\cdot}00\times10^{-14}\ mol^2\ L^{-2}$$

$$pH+pOH=pKw=14 \text{ at } 298K$$

The pH and pOH of any solution are related to one another as follows :

$$pH+pOH=14$$

So, if either the pH or pOH of a solution is known, the other can be found by substracting from 14.

To differentiate between neutral, acidic and basic solutions, one can make this distinction in terms of pH,

| pH | | $[H_3O^+]$ | $[OH^-]$ | |
|---|---|---|---|---|
| $>7{\cdot}0$ | Basic | $<10^{-7}$ | $>10^{-7}$ | mol $L^{-1}$ |
| $=7{\cdot}0$ | Neutral | $10^{-7}$ | $10^{-7}$ | mol $L^{-1}$ |
| $<7{\cdot}0$ | Acidic | $>10^{-7}$ | $<10^{-7}$ | mol $L^{-1}$ |

There are no upper or lower limits to the pH scale, but for the vast majority of practical applications pH values are in the range 0 to 14.

For example, if a solution contains $4{\cdot}6\times10^{-3}$ mol $L^{-1}$ of $[H_3O^+]$ ions, its pH would be obtained as follows :

$$
\begin{aligned}
pH &= -\log\,[H_3O^+]\\
&= -\log\,[4{\cdot}6\times10^{-3}]\\
&= -[\log 4{\cdot}6+\log 10^{-3}]\\
&= -[0{\cdot}66-3]\\
&= 2{\cdot}34
\end{aligned}
$$

There are many situations that require that we convert measured pH values to hydrogen ion or hydroxide ion concentrations. For example, if a solution has pH 5.85, its hydrogen ion concentration would be,

$$
\begin{aligned}
pH &= -\log\,[H^+]\\
[H^+] &= \text{Antilog of} - pH\\
&= \text{Antilog of} - (5{\cdot}85)\\
&= \text{Antilog}\,(0{\cdot}15-6)\\
[H^+] &= 1{\cdot}41\times10^{-6}\ M
\end{aligned}
$$

Thus, the nature of the solution can be known by knowing the pH value of the solution. Acidity and basicity on the pH scale are as given in Fig. 15.1.

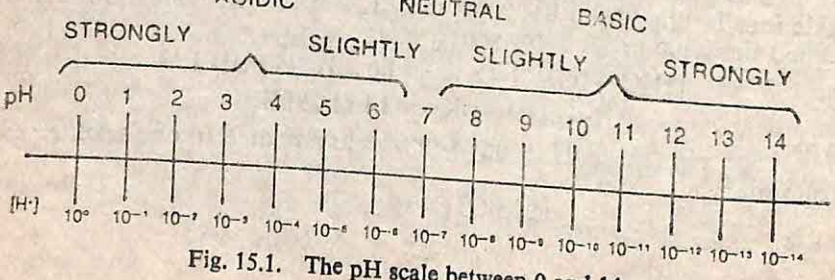


Fig. 15.1. The pH scale between 0 and 14.

## 15.2. Determination of pH

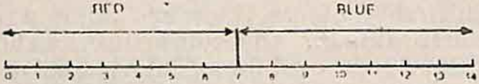
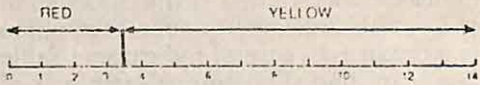
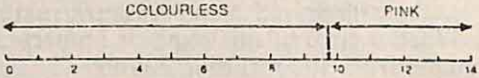
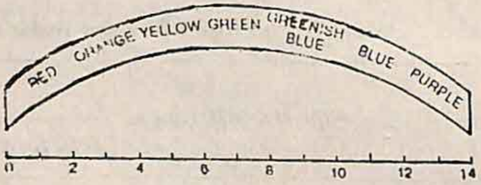
The pH of solution can be easily determined by using a universal indicator paper. The basic principle of the indicator paper is that it experiences a change in colour which is characteristic of the pH of the test sample of the solution. Organic substances which show distinctly different colours below and above a small pH range are called *indicators*. It is very difficult to make a choice as regards the particular indicator to be used for an unknown solution. Therefore, we must use an indicator which gives distinctly different colours over a wide range of pH. This indicator is none other than the universal indicator which is a mixture of several indicators (Table 15.1). With such a solution one can find the approximate pH of any solution within this range. So called, pH paper is impregnated with a universal indicator. When a strip of this paper is immersed in a solution the pH can be judged from the resulting colour.

**Table 15.1. Working range of some indicators**

| *Indicator* | *Effective pH range* | *Colour* | |
|---|---|---|---|
| | | *Acid form* | *Base form* |
| Methyl violet | 0·0—3·0 | Yellow | Violet |
| Methyl orange | 2·1—4·4 | Red | Yellow |
| Methyl red | 4·2—6·2 | Red | Yellow |
| Bromothymol blue | 6·0—7·8 | Yellow | Blue |
| Phenol red | 6·8—8·4 | Yellow | Red |
| Thymol blue | 7·9—9·4 | Yellow | Blue |
| Phenolphthalein | 8·3—10·0 | Colourless | Red |
| Alizarin yellow | 10·1—12·1 | Yellow | Red |

The colour an indicator shows, when you add it to a solution, depends on the pH of the solution. So you can use indicators to give you an idea of pH of any solution. Table 15.2 shows the different colours.

**Table 15.2. How indicators change colour with pH**

| *Indicator* | *Colour of indicator at different pH values* | *Colour change* |
|---|---|---|
| Litmus |  RED<br>BLUE<br>0<br>1<br>2<br>3<br>4<br>5<br>6<br>7<br>8<br>9<br>10<br>11<br>12<br>13<br>14 | Red↔Blue at pH 7 |
| Methyl orange |  RED<br>YELLOW<br>0<br>1<br>2<br>3<br>4<br>6<br>8<br>10<br>12<br>14 | Red↔Yellow at pH 3·4 |
| Phenol-phthalein |  COLOURLESS<br>PINK<br>0<br>2<br>4<br>6<br>8<br>10<br>12<br>14 | Colourless ↔Pink at pH 9·8 |
| Universal indicator |  RED<br>ORANGE<br>YELLOW<br>GREEN<br>GREENISH BLUE<br>BLUE<br>PURPLE<br>0<br>2<br>4<br>6<br>8<br>10<br>12<br>14 | Series of colour changes through the whole range |

**Experiment 15.1.** To determine the pH value of the following solutions using universal indicator paper and to classify them as acid, neutral or alkaline : (*i*) tap water, (*ii*) distilled water (*iii*) lemon juice (*iv*) vinegar (*v*) milk, (*vi*) lime water (*vii*) tomato juice (*viii*) orange juice (*ix*) dilute $H_2SO_4$, (*x*) dilute NaOH, etc.

**Apparatus.** Beakers, test tubes, funnel, filter paper, dropper.

**Chemicals.** Universal indicator paper, solutions of test samples, pH chart.

**Procedure.** (*i*) Prepare the test solutions of acids and bases by taking them from shelf of various dilutions (concentrations). Extrect the juice from lemon/orange/pine apple/tomato, etc.Now take all these samples in test tubes and number them carefully with their names.

Make small pieces of the universal indicator paper and place these on a glazed tile and number them 1 to 10.

(*iii*) Take a clean dropper and put one drop of tap water on indicator paper no. 1 and match the colour obtained with the standard colour chart. Note the pH on the colour chart where the two colours match. Now similar to this take all the solutions one by one provided to you (or prepared by you) with the help of clean droppers and put them on separate indicator papers placed on the tile. Again match the colour developed on the pH paper with the standard pH chart and thus note the pH of the various solutions.

(*iv*) Record your observations as suggested in the table given below and classify them as acidic, neutral or alkaline.

**Note**. In case the universal indicator paper is not available, add 2-3 drops of universal indicator solution in all the test solutions contained in various test tubes.

**Observations**

| *S. N.* | *Sample solution test tube* | *pH value* | *Acidic/neutral/ alkaline* |
|---|---|---|---|
| 1. | Tap water | | |
| 2. | Distilled water | | |
| 3. | Lemon juice | | |
| 4. | Vinegar | | |
| 5. | Milk | | |
| 6. | Lime water | | |
| 7. | Tomato juice | | |
| 8. | Orange juice | | |
| 9. | Dilute $H_2SO_4$ | | |
| 10. | Dilute NaOH | | |

## 15.3. Effect of Common Ion on pH

Consider the ionization of aqueous acetic acid,

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

This is the equilibrium for the ionization of acetic acid in water. However, the solution that we are considering differs from a solution of acetic acid in water, in that it has a large concentration of acetate ion as well as acetic acid.

In this case, the expression for the equilibrium constant, $K_a$ is

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad \text{...(15.1)}$$

When sodium acetate having a common acetate ion is added to this, it is almost completely ionized as follows :

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Therefore, the addition of sodium acetate results in an increase in the concentration of $CH_3COO^-$ ions. Henec, to maintain the value of $K_a$ constant in equation (15.1), the concentration of $[CH_3COOH]$ will be increased and the concentration of $(H_3O^+)$ decreased proportionally, because some of the $CH_3COO^-$ will recombine with $H_3O^+$ forming $CH_3COOH$. Thus, the addition of $CH_3COONa$ to acetic acid suppresses the ionization of acetic acid and this decreases the concentration of $H_3O^+$ ions in the solution. The decrease in the concentration of $H_3O^+$ ions results in an increase in the value of pH. The suppression in the degree of dissociation of a weak electrolyte (acetic acid) in solution on addition of an electrolyte solution which has an ion in common is an example of the **common ion effect.**

Ammonium hydroxide (a weak base) ionizes in water as given,

$$NH_4OH \rightleftharpoons NH^{4+} + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad .. (15.2)$$

When ammonium chloride solution having a common ammonium ion is added to this solution, it furnishes $NH_4^+$ and $Cl^-$ ions on ionization,

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Therefore, on addition of ammonium chloride an increase in the concentration of the $NH_4^+$ ions takes place. Hence, to maintain the value of $K_b$ constant in Equation (15.2), the concentration of $NH_4Cl$ will be increased and the concentration of $OH^-$ decreased proportionally, because some of $NH_4^+$ ions will recombine with $OH^-$ ions to form $NH_4OH$. Thus, the addition of $NH_4Cl$ to $NH_4OH$ solution suppresses the ionization of $NH_4OH$ and this decreases the concentration of $OH^-$ ions in the solution. As the $OH^-$ ions concentration is decreased, the $H^+$ ions concentration will proportionally increase because the value of $K_w$ is constant, *i e.*,

$$K_w = [H^+][OH^-] = 10^{-14}$$

The increase in the concentration of $H^+$ ions results in a decrease in the pH of the solution.

**Experiment 15.2.** To study the pH change by common ion effect in case of weak acids and weak bases.

**Apparatus.** Test tubes, droppers.

**Chemicals.** Universal indicator paper, pH chart, distilled water, sodium acetate, acetic acid, ammonium chloride and ammonium hydroxide (aqueous ammonia solution).

**Procedure**

1. **Acidic Solution.** Take two test tubes A and B. Take about 2-4 mL of dilute acetic acid in both the tubes. Now add 0.5-1 g of sodium acetate to the test tube B and shake it well. Put two drops from each of the tubes on separate indicator papers placed on a glazed tile. Match the colour obtained with the standard colour chart. Note down the pH value.

2. **Basic Solution**. Follow the above procedure by taking pure 2-4 mL of dilute solution of ammonium hydroxide (aqueous ammonia) in test tube A and a mixture of aqueous ammonia (2-4 mL) and ammonium chloride (0 5-1 g). Note the colour developed and determine the pH by comparing them with the standard pH chart.

**Observations**

| *Solution* | *pH value* |
|---|---|
| 1. (*i*) acetic acid | |
| (*ii*) Homogeneous solution of acetic acid plus sodium acetate. | |
| 2. (*i*) Aqueous ammonia ($NH_4OH$) | |
| (*ii*) Homogeneous solution of aqueous ammonia plus ammonium chloride. | |

**Result**. 1. The pH of acetic acid solution increases on adding a strong electrolyte (sodium acetate) to it.

2. The pH of aqueous ammonia decreases on adding a strong electrolyte (ammonium chloride) to it.

## ORAL QUESTIONS AND ANSWERS

**Q. 15.1.** Define (*i*) an acid, and (*ii*) a base.

**Ans.** (*i*) An acid is a substance that yields hydroxinium ions or aqueous hydrogen ions ($H_3O^+$) as the only positive ions in aqueous solution.

(*ii*) A base is a substance that yields hydroxide ions ($OH^-$) as the only negative ions in aqueous solution.

**Q. 15.2.** What is pH ?

**Ans.** Refer to section 15.1.

**Q. 15.3.** What is meant by the pH of a solution ?

**Ans.** Degree of acidity.

**Q. 15.4.** Define the term (*i*) neutral, and (*ii*) neutralization.

**Ans** (*i*) Neutral means that the concentrations and amounts of $H^+$ ($H_3O^+$) and $OH^-$ ions are equal (*ii*) The mixing of solutions of $H_3O^+(aq)$ and $OH^-(aq)$ resulting in equal concentrations of each at the neutral point ($pH=7$).

**Q. 15.5.** Explain how the degree of acidity of different solutions is expressed and give two common examples.

**Ans.** $pH, = -\log [H_3O^+(aq)]$

=minus log of the hydroxonium ion concentration

Measured by a pH meter or universal indicator paper.
Lime juice pH=1·3
Baking powder solution pH=8·7.

**Q. 15.6.** What is universal indicator ?

**Ans.** This is a mixture of several indicators dissolved in absolute alcohol. It changes colour continuously over a wide pH range.

**Q. 15.7.** What is the approximate pH of the following solutions ?

(*i*) sea water (*ii*) blood (*iii*) saliva (*iv*) bile (*v*) cow's milk (*vi*) gastric juice.

**Ans.** (*i*) Sea water : 8·5 (*ii*) Blood : 7·4
(*iii*) Saliva : 6·8 (*iv*) Bile : 7·8
(*v*) Cow's milk : 6·6 (*vi*) Gastric juice : ~1·0

**Q. 15.8.** What will be the pH of 0.1 NHCl solution ?

**Ans.** The pH of 0·1 NHCl is 1.

**Q. 15.9.** What is the pH of a pure sample of water at 298K ?

**Ans.** Theoretically it is 7·0. However, it is always found to be a little less than 7·0 when measured by a pH meter.

**Q. 15.10.** What is a buffer solution ?

**Ans.** A solution that has the ability to maintain a very nearly constant pH even when moderate amounts of acid or base are added to it is called a buffer solution.

**Q. 15.11.** Addition of $NH_4Cl$ decreases the pH of a solution of aqueous ammonia. Comment.

**Ans.** Refer to section 15.3,

**Q. 15.12.** A solution of sodium acetate and acetic acid in approximately equal proportions act as a buffer solution'. Explain.

**Ans.** If $H_3O^+$ is added to the acetate-acetic acid buffer solution, it combines almost completely with $CH_3COO^-$ forming $CH_3COOH$

$$CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O$$

Therefore, there is no appreciable change in the $H_3O^+$ concentration and the pH remains unaltered.

If $OH^-$ is added to the acetate-acetic acid buffer solution, it combines almost completely with acetic acid, converting it to acetate ion,

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

So, again there is no change in the $OH^-$ (or $H_3O^+$) concentration, and therefore, in the pH.

**Q. 15.13.** Calculate (*a*) the pH of a solution of $[H^+]=0{\cdot}001$ M. (*b*) the pH of a solution of $[OH^-]=10^{-9}$ M.

**Ans.** $$[H^+]=0{\cdot}001\ M=\frac{1}{1000}\ M$$
$$=10^{-3}\ M$$

Therefore, $$pH=-\log 10^{-3}=3$$

(*b*) $$[OH^-]=10^{-9}\ M$$
$$[H^+]\times[OH^-]=1\times10^{-14}$$

or $$[H^+]=\frac{1\times10^{-14}}{[OH^-]}=\frac{1\times10^{-14}}{10^{-9}}$$
$$=10^{-14+9}=10^{-5}\ M$$
$$pH=-\log[H^+]=-\log 10^{-5}=5.$$

**Q. 15.14.** Calculate (*a*) $[H^+]$, and (*b*) $[OH^-]$ of a solution of pH=4.

**Ans.** $$pH=-\log[H^+]=\log\frac{1}{[H^+]}$$
$$4=-\log[H^+]=\log\frac{1}{[H^+]}$$

or $$\log\frac{1}{[H^+]}=4=\log 10^4$$

Taking antilog on both sides,
$$\frac{1}{[H^+]}=10^4$$

or $$[H^+]=\frac{1}{10^4}=10^{-4}\ M$$

**Q. 15.15.** Identify each of the following solutions as acidic, basic or neutral

(*a*) pH=2 (*b*) pOH=6 (*c*) pH=9
(*d*) pOH=14 (*e*) $[H^+]=10^{-7}$M (*f*) pOH=9
(*g*) pH=0 (*h*) pH=3·5 (*i*) $[H^+]\geqslant10^{-7}$M
(*j*) $[OH^-]=10^{-7}$M (*k*) pH=11·3 (*l*) $[OH^-]\leqslant10^{-7}$M
(*m*) pOH=2·7 (*n*) pOH=13 (*o*) $[OH^-]\geqslant10^{-7}$M
(*p*) $[H^+]\leqslant10^{-7}$M (*q*) pH=7 (*r*) pOH=7

[**Ans.** Acidic : *a, d, f, g, h, i, l, n*
Basic : *b, c, k, m, o, p*
Neutral : *e, j, q, r*].

□ □

# UNIT 16

# The Rates of Chemical Reactions

## 16.1. Introduction

**The meaning of rate.** It is faster to use the lift, slower to use the stairs. The word fast and slow both describe the rate of going up or coming down. Rate is a measure of the 'change' that happens in a single unit of time. The unit of time can be a second, a minute or an hour. Many different rates of change are used in everyday life. A few examples are listed in Table 16.1.

**Table 16.1. Some everyday experiences with rates of change**

| | *Example* | *Rate* |
|---|---|---|
| 1. | Going to school by bus | 30 kilometers per hour (km ph) |
| 2. | Going to school by train | 60 kilometers per hour (km ph) |
| 2. | Playing a long playing (LP) record | 30 revolutions of the turntable per minute (rpm) |
| | Playing a single | 50 revolutions of turntable per minute (rpm) |
| 3. | Pouring petrol from a hand operated pump | 50 mL per second |
| | Pouring petrol from a electricity operated pump | 500 mL per second |

### Rate of Chemical Change

In n chemical change reactants change to products. Chemical reactions vary enormously in speed. Some proceed slowly over a period of months (*e.g.*, the rusting of iron); others take week to reach completion (*e.g.*, the fermentation of alcohol); some reactions are very fast (*e.g.*, neutralization reaction of a strong acid and a strong base ; precipitation of insoluble salts) ; others are so fast as to be explosive (*e.g.*, the reaction between hydrogen and oxygen).

The speed of a reaction is called its rate.

We have seen that different reactions occur with different speeds. In every reaction, the concentration of reactants decreases and the concentration of products increases with time. The speed at which a reaction takes place can be expressed as the **rate of reaction**. The rate of a chemical reaction is defined as the change in concentration of reactants or products per unit time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

For example, a reactant with concentration 4·0 moles/litre decomposes into products. After 10 minutes its concentration is measured to be 2·4 moles/litre. The rate of the decomposition reaction is given by,

$$\text{Rate} = \frac{(4{\cdot}0 - 2{\cdot}4)\ \text{moles per litre}}{10\ \text{minutes}}$$

$$= \frac{1{\cdot}6}{10}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$= 0{\cdot}16\ \text{mol L}^{-1}\ \text{min}^{-1}.$$

### Measuring rates

The next important question is : how can amounts of reactants or products be measured ? This is often not easy to answer. In most of the reactions, reactants and products stay all mixed up, and in the same state.

In the reaction,

$$\text{NaOH}(aq) + \text{HCl}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

all the reactants and products are in the same state (or phase). This is called a homogeneous reaction.

To separate one of them and measure the amount of it can be difficult.

In this unit, we shall look only at reactions that give a products in a different state from the reactants. Because the product is in a different state (or differs in colour from the reactant, etc.) the amount of it can usually be measured easily.

### Factors that affect rate

We have seen that reactions move with different speeds. The rate of a reaction depends upon the following factors :

(*i*) concentration, (*ii*) pressure, (*iii*) temperature, (*iv*) light, (*v*) surface area, and (*vi*) catalyst.

(*i*) An increase in the concentration of reactants produces an increase in the reaction rate. This holds true for most of the reactions.

(*ii*) As the concentration is a measure of the number of particles in a unit volume, an increase in pressure (particularly if the reactants are gases) leads to an increase in concentration. This in turn leads to an increase in the rate of reaction.

(*iii*) The reaction rate increases as the temperature increases. While the effect of concentration on rate is being studied, the temperature of the system is always held constant and *vice versa*.

(*iv*) Most of the reactions you perform in the laboratory are unaffected by light. Reactions that are speeded up by light are called photochemical reactions, *e.g.*, a mixture of hydrogen and chlorine gases explode when exposed to light. Photochemical reactions are not very common.

(*v*) The reaction rate increases when the surface area of the reactants is increased. Reaction of acid on powdered marble is much faster than on marble in chips form.

(*vi*) A catalyst, generally, increases the rate of a reaction, *e.g.*, synthesis of ammonia from $N_2$ and $H_2$ is catalyzed by iron.

Now we shall plan a few experiments for studying the effect of concentration and temperature on the rate of reaction.

## 16.2. Experiments

**Experiment 16.1.** To measure the effect of concentration on the rate of chemical reaction.

$$H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$$

at room temperature using different concentrations of iodide ions.

**Apparatus.** Beakers, conical flasks, burette, stop clock, measuring flasks.

**Chemicals.** $H_2O_2$, KI, $H_2SO_4$, starch solution.

**Chemical reaction and basic principle**

In acidic solution,

$$2I^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O + I_2$$

It is quite likely that some HI would be formed in the reaction. The HI so produced, in turn, would react with unreacted $H_2O_2$ forming molecular iodine.

Molecular iodine reacts with starch present in the solution to give the blue coloured compound that colours the solution.

**Procedure.** (*i*) Prepare 250 mL 1 M $H_2O_2$ solution. Measure out $H_2O_2$ solution in five beakers so that each contains 25 mL. Now put these beakers in a trough containing cold water.

(*ii*) Prepare 250 mL 2 M KI solution. Using a burette, measure out five different volumes say 25, 20, 15, 10 and 5 ml of KI solution in five conical flasks marked as 1, 2, 3, 4 and 5. Add distilled water in conical flasks marked 2, 3, 4 and 5 so that the total volume in each flask is the same. Now add 2 mL of dilute $H_2SO_4$(4N) and 10 drops of freshly prepared starch solution. Shake the solutions in the flasks. Put the flasks in a trough containing cold water.

(*iii*) Make a cross on a piece of paper, with a pencil.

Put the paper under the flask no. 1 containing the KI solution, so that you can see the cross through the liquid.

(*iv*) Now pour the $H_2O_2$ solution into the KI solution (flask no. 1). Start a stop watch at the same time. Swirl the solution in the flask.

(*v*) Determine the time from the moment of the addition of the $H_2O_2$ solution to the moment the cross completely disappears.

(*vi*) As the blue suspension forms, it blots out the cross from view. Stop the stopwatch the moment the cross completely disappears.

(*vii*) Repeat the operation with the remaining four flasks.

(*viii*) Plot a graph of concentration of KI solution (this is to be calculated, or just use the volumes of KI solution used) against time. The shape of graph will be as given in Fig. 16.1.

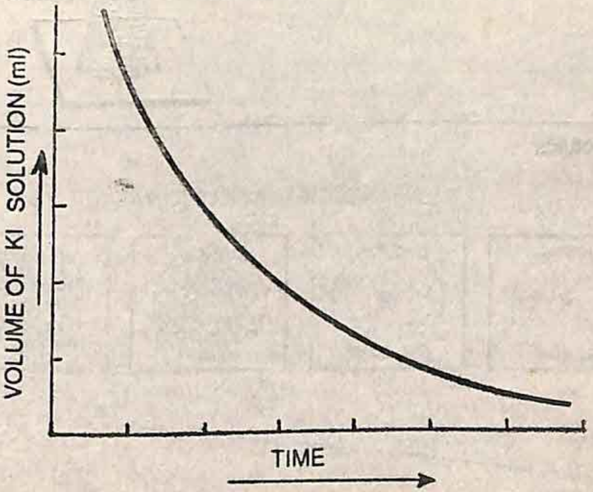
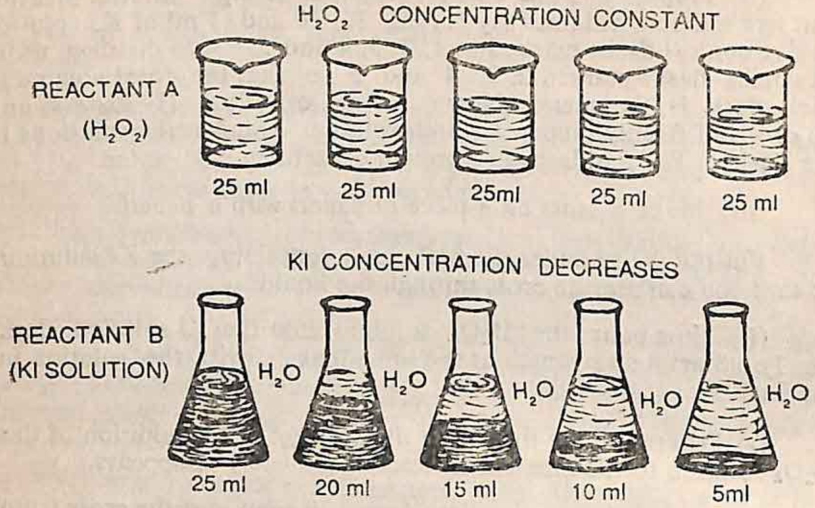


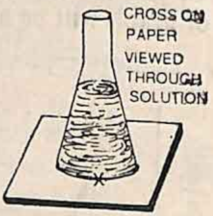
**Fig. 16.1.** Concentration-time curves for the reaction of KI with $H_2O_2$ at room temperature.

**Observations**

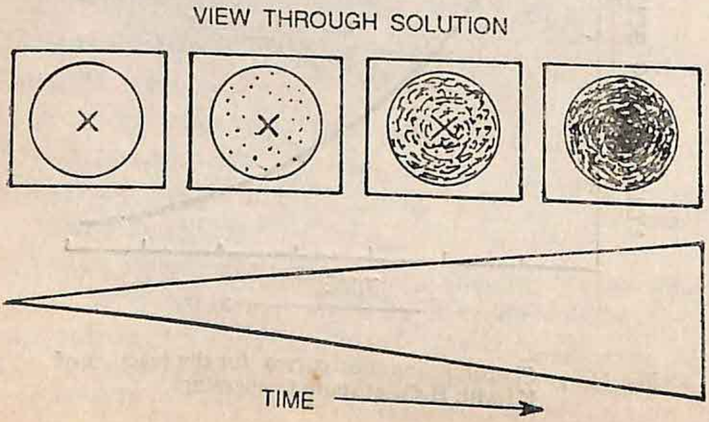


(*i*) Water is added to keep the volume constant
(*ii*) Equal volume of $H_2SO_4$ and starch solution is also added.

Time taken for mark to disappear



Rate decreases



Time taken for mark to disappear increases

**Results and Discussion**

The longer it takes for the mark to disappear, the slower the rate. With the use of the same volume of $H_2O_2$ solution and the same volume of KI solution, you will always have the same volume of solution when you mix them together. The addition of starch monitors the progress of reaction. Starch on reacting with molecular iodine forms insoluble blue coloured complex. The cross will always disappear when a certain number of blue coloured complex particles have formed in the fixed volume. So it amounts to measuring the time it takes to produce a certain amount of complex.

As you see from the trend of the time taken the rate of the reaction is the highest when the concentration of reactant B (KI) is the highest. Thus, the more reactant there is present, the faster the reaction will go.

**Note**. The procedure can be made more effective by adding 1 mL of 0·1% solution of sodium thiosulphate to each of the flasks along with the KI solution, etc. When you add $H_2O_2$ solution to the mixture of iodide ions, sodium thiosulphate, acid and starch, the iodide ions react with $H_2O_2$ to liberate iodine.

$$2KI(aq)+H_2SO(aq)+H_2O_2(aq) \longrightarrow K_2SO_4(aq)+2H_2O(l)+I_2(aq)$$

But this iodine immediately reacts with $Na_2\ S_2O_3$ solution :

$$I_2(aq)+S_2O_3^{2-}(aq) \longrightarrow 2I^-+S_4O_6^{2-}(aq)$$

and this continues to happen until all the $S_2O_3^{2-}$ ions have been used up. Then the iodine reacts with the starch solution to give blue colour. Determine the time from the moment of the addition of $H_2O_2$ to the moment when the solution turns blue.

In this case, it is not necessary to observe the blotting of the cross. When $H_2O_2$ solution is added start a stop-clock, cork the flask, quickly shake it and put it in the trough. Stop the clock as soon as a blue colouration appears in the flask. Record the time.

In the absence of sodium thiosulphate, one has to solely depend upon the appearance of blue colour. The addition of $Na_2S_2O_3$ increases the time of reaction and appearance of blue colour signals a certain stage of the reaction.

**Experiment 16.2**. To study the reaction rates between potassium iodate and sodium sulphite using starch indicator at different concentrations and temperatures.

**Apparatus**. Beakers, conical flasks, stop clock, burette, measuring flasks, thermometers, boiling tubes, stirrers.

**Chemicals**. Potassium iodate, sodium sulphite, starch sulphuric acid.

### Chemical reaction and basic principle

Oxidation of sodium sulphite with potassium iodate is expressed by this equation.

$$2KIO_3+5Na_2SO_3+H_2SO_4 \longrightarrow I_2+K_2SO_4+5Na_2SO_4+H_2O$$

This reaction proceeds in steps :

$$Na_2SO_3+H_2SO_4 \longrightarrow H_2SO_3+Na_2SO_4$$

$$KIO_3+3H_2SO_3 \longrightarrow KI+3H_2SO_4$$

$$KIO_3+3H_2SO_4+5KI \longrightarrow 3K_2SO_4+3H_2O+3I_2$$

$$I_2+\text{Starch} \longrightarrow \text{Starch}-I_2 \text{ (blue in colour)}$$

### Effect of concentration (temperature constant)

**Procedure**. (*i*) Prepare 250 mL 1 M solutions of potassium iodate and sodium sulphite.

(*ii*) Using a burette, measure out, five different volumes say 25, 20, 15, 10 and 5 mL of $KIO_3$ solution in five conical flasks labelled as 1, 2, 3, 4 and 5. Make up the total volume 25 mL in each of them by adding distilled water.

(*iii*) Take 25 mL of sodium sulphite solution in five beakers. Put 1 mL of dilute $H_2SO_4$ to each one of them followed by 10 drops of starch solution.

(*iv*) For the operation, follow the procedure as suggested in experiment no. 16.1.

### Effect of temperature (concentration constant)

**Procedure.** (*i*) Prepare five water baths Nos. 1, 2, 3, 4 and 5. To that end, fill five 250 mL beakers with waler to ½ of their capacity. Keep one beaker on the table at room temperature. Measure thet emperature of water with thermometers. Heat water in two beakers say No. 4 and 5 to temperatures 10°C and 20°C above the room temperature respectively. Adjust the flame of the burners so the water temperature remains almost constant (±0·5°C). Cover each beaker with a lid provided with four holes. Place a stirrer in one hole, a thermometer reading to 50° or 100°C in another hole, and the remaining two holes are to be used for the reactants.

(*ii*) In the mean time, prepare 250 mL 1 M solutions of potassium iodate and sodium sulphate.

(*iii*) Now using a burette measure out five equal volumes say 20 mL of $KIO_3$ solution in five boiling tubes labelled as 1, 2, 3, 4 and 5. Insert tube No. 1 in one of the holes provided in the waterbath No. 1. Put the remaining tubes in the other waterbaths.

(*iv*) Pour 20 mL sodium sulphite solution into five different boilings tubes. Now add 1 mL of dilute $H_2SO_4$ to each one of them followed by 10 drops of starch solution. Put these boiling tubes in five different waterbaths.

(*v*) Now take the waterbath No. 1 and maintain its temperature at 0°C by adding ice. Now add $KIO_3$ solution from the boiling tube in water bath No. 1 to the test tube containing sodium sulphite solution in the same waterbath. Shake the tube well.

(*vi*) Determine the time that elapses from the moment when the $KIO_3$ is added to the moment when the solution turns blue.

(*v*) Now maintain the temperatures in different waterbaths as given in table and repeat the operation in these waterbaths also. Determine the time of reaction as described for waterbath No. 1.

**Observations**

The experiment and its results.

---

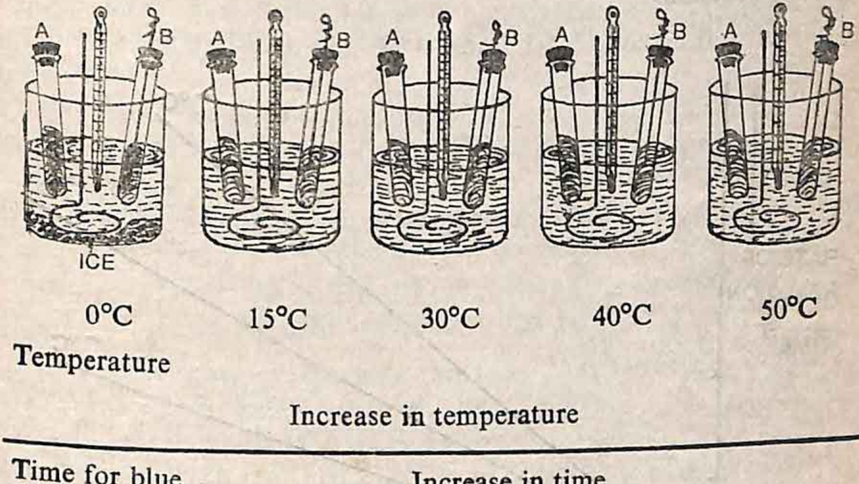
Reactants : (constant concentration) (in water baths)

A—20 mL $KIO_3$ solution

B—20 mL $Na_2SO_3$ solutlon

1 mL $H_2SO_4$

10 drops starch



| | |
|---|---|
| Temperature | 0°C  15°C  30°C  40°C  50°C<br>Increase in temperature |
| Time for blue colour to appear | Increase in time<br>←———— |
| Rate of reaction, $\frac{1}{\text{Time}}$ $s^{-1}$ | Increase in time<br>←———— |

Perform the experiment at different concentration of $KIO_3$ solution and tabulate the observations and experimental results as given on next page :

| S. No. | Volume of $KIO_3$ solution (mL) | Volume of water added (mL) | Concentration of $KIO_3$ solution | Time for blue colour to appear | | | Rate of reaction (measured as $\frac{1}{Time}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | | Room t°C | 40°C | 50°C | |
| 1 | 25 | – | | | | | |
| 2 | 20 | 5 | | | | | |
| 3 | 15 | 10 | | | | | |
| 4 | 10 | 15 | | | | | |
| 5 | 5 | 20 | | | | | |

Plot the graph of $KIO_3$ volume (or concentration) against rate of reaction.

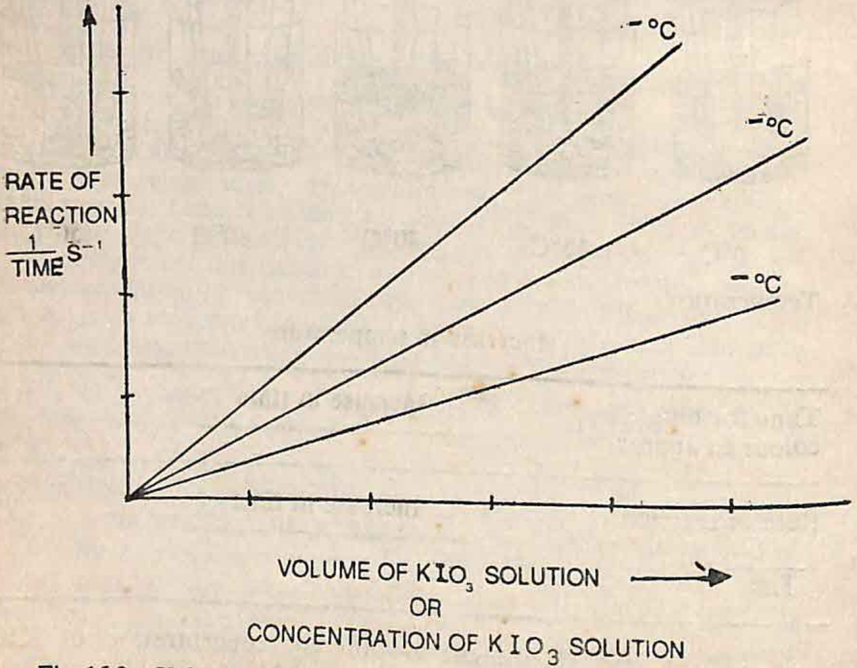


Fig. 16.2. Volume of $KIO_3$ solution or concentration of $KIO_3$ solution.

**Results and Discussion**

From the observations and the graph you will see that the reaction rate increases as the temperature increases. Also as the concentration is increased the rate of reaction increases.

**Note**

(*i*) With the use of thermostat better results will be expected.

(*ii*) Time for cross (drawn on a piece of paper as suggested in experiment 16.1) to disappear can also be measured. In that case, it is advised is to carry out the reaction in a small conical flask, so that the visibility of cross is not hampered by the column of solution as in the case of boiling tube.

(*iii*) Along with starch, solution of sodium thiosulphate can also be added to increase the reaction period. Initially blue colour will not appear as the liberated molecular iodine will be consumed by sodium thiosulphate. Blue colour will appear only, after the reaction between $Na_2S_2O_3$ and $I_2$ is over.

## ORAL QUESTIONS AND ANSWERS

**Q. 16.1.** What do you understand by the rate of reaction.

**Ans.** Refer to section 16.1.

**Q. 16.2.** What are the factors which could affect the rate of reaction.

**Ans.** Refer to section 16.1.

**Q. 16.2.** What are homogeneous and heterogeneous reactions ?

**Ans.** Homogeneous reactions are those in which the reactants and products are in the same phase. For example,

$$NaOH\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

$$H_2\,(g) + Cl_2\,(g) \longrightarrow HCl\,(g)$$

Heterogeneous reactions are those in which the reactants and products are in different phases. For example.

$$2Mg\,(s) + O_2\,(g) \longrightarrow 2MgO\,(s)$$

$$Zn\,(s) + 2HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

# UNIT 17

# Chemical Equilibrium

## 17.1. Introduction

All chemical reactions carried out in a closed system eventually reach a state of equilibrium in which the concentrations of all the reactants and products do not change with time. In a closed system, none of the products are removed or allowed to escape from the reaction vessel, and no additions of any of the reactants are made. The equilibrium is always a dynamic one, in that the reaction does not stop when equilibrium has been attained, but the rate of the forward reaction decreases while that of the reverse reaction increases to the point at which the rates of the forward and reverse reactions are equal.

The reactants and the products do not always have the same equilibrium concentration. In fact, equilibrium concentrations depend on the initial concentrations of the reactants and the products, and on the temperature. The quantitative treatment of equilibrium concentrations is governed by the law of chemical equilibrium, sometimes called the law of mass action and mathematically described as the equilibrium expression.

Consider a reversible reaction $A+B \rightleftharpoons C+D$

Applying the law of mass action,

The rate of the forward reaction, $V_f$

$$V_f \propto [A][B] = K_f [A]\ [B] \qquad (16.1)$$

The rate V of the reverse reaction, $r_r$

$$V_r \propto [C]\ [D] = K_r [C]\ [D] \qquad (16.2)$$

where $K_f$ and $K_r$ are the rate constants of the forward and the reverse reactions respectively.

At equilibrium $\quad r_f = r_r$

Hence, $\quad K_f [A]\ [B] = K_r\ [C]\ [D]$

or

$$\frac{K_f}{K_r} = \frac{[C]\ [D]}{[A]\ [B]} = K_c \qquad (16.3)$$

$K_c$ which is equal to the ratio of the two rate constants, is called the equilibrium constant. The equation (16.3) is called the equilibrium expression.

In general, in an equilibrium

$$aA+bB \rightleftharpoons cC+dD$$

$$K_c=\frac{[C]^c\,[D]^d\text{ (products)}}{[A]^a\,[B]^b\text{ (reactants)}}$$

## 17.2. The Effect of Conditions on the Position of Equilibrium

Le Chatelier studied the influence of pressure, temperature and concentration on equilibria. His views are known as Le Chatelier's principle. This states that in any equilibrium when a change is made in the concentration, temperature or pressure of an equilibrium mixture, the equilibrium shifts in direction that tends to oppose the change.

Now we shall discuss the effect of these factors on equilibrium state of a reaction.

### 17.2.1. Effect of Change of Concentration

Consider the following equilibrium

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

Suppose some $H_2$ is added to the equilibrium, the equilibrium will shift towards right. Similarly, addition of $N_2$ causes a shift to the right, and addition of $NH_3$ causes a shift to the left. The general rule is that increase in the concentration of one substance in an equilibrium mixture displaces the equilibrium in that direction which consumes some of the added material. Decrease in the concentration of a substance causes the production of more and more of that substance. This property is utilized in chemical industries to get better yield.

### 17.2.2. Effect of Change in Temperature

Consider the following reaction at equilibrium,

$$N_2(g)+3H_2(g) \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2NH_3(g)+92\text{kJ}$$

The forward reaction is exothermic and the reverse reaction is endothermic. In applying Le Chatelier's principle to predict the effect of change in temperature on the equilibrium, the general rule is, increase in the temperature causes reaction to occur in that direction which results in absorbtion of heat, and decrease in the temperature causes reaction to occur in the direction which results in the evolution of heat. Therefore, decrease of temperature in the above reaction shifts equilibrium towards right, *i.e.*, favours formation of ammonia.

Similarly, in reaction

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g)-180{\cdot}5\text{ kJ}$$

if temperature is increased the forward reaction is favoured. Now we conclude that formation of ammonia is favoured at low temperature and formation of nitric oxide is favoured at high temperature.

| | *Forward reaction* | *Reverse reaction* | *Favoured by increased temperature* | *Favoured by decreased temperature* |
|---|---|---|---|---|
| 1. | exothermic | endothermic | reverse | forward |
| 2. | endothermic | exothermic | forward | reverse |

### 17.2.3. Effect of Change in Pressure

The rule is that increase in the pressure on the reaction in equilibrium favours that reaction which produces less moles of gas. For example, the combination of sulphur dioxide and oxygen to give sulphur trioxide

$$\underbrace{2SO_2(g)+O_2(g)}_{2+1=3\text{ moles}} \rightleftharpoons \underbrace{2SO_3(g)}_{2\text{ moles}}$$

is accompanied by a decrease in number of moles. According to Le Chatelier's principle, therefore, a high pressure would give a better yield of sulphur trioxide. Similarly, the formation of ammonia

$$\underbrace{N_2(g)+3H_2(g)}_{1+3=4\text{ moles}} \rightleftharpoons \underbrace{2NH_3(g)}_{2\text{ moles}}$$

is accompanied by a decrease in the number of moles. If the pressure is increased volume will decrease. Thus, increase in production of ammonia is observed at higher pressure.

Consider the dissociation of phosphorus pentachloride,

$$\underbrace{PCl_5(g)}_{1\text{ mole}} \rightleftharpoons \underbrace{PCl_3(g)+Cl_2(g)}_{1+1=2\text{ moles}}$$

The forward reaction is accompanied by the increase in number of moles. According to Le Chatelier's principle the dissociation of phosphorus pentachloride is suppressed with increase of pressure.

Other reactions that illustrate the effect of change in pressure are the following :

| *Reaction* | *Direction favoured by increased pressure* |
|---|---|
| $C(s)+H_2O(g) \rightleftharpoons CO(g)+H_2(g)$ | reverse (←) |
| $2NO_2(g) \rightleftharpoons N_2O_4(g)$ | forward (→) |
| $H_2(g)+Cl_2(g) \rightleftharpoons 2HCl(g)$ | neither |

The following table summarizes the effects on the synthesis of ammonia discussed in this section :

| *Change* | *Reaction favoured* |
|---|---|
| add $N_2$ or $H_2$ | forward (→) |
| add $NH_3$ | reverse (←) |
| remove $N_2$ or $H_2$ | reverse (←) |
| remove $NH_3$ | forward (→) |
| increase pressure | forward (→) |
| decrease pressure | reverse (←) |
| increase temperature | reverse (←) |
| decrease temperature | forward (→) |

## 17.3. Experiments

**Experiment 17.1.** To study the shift in equilibrium between ferric ions and thiocyanate ions by increasing the concentration of either ions.

**Apparatus.** Beaker, boiling tubes, boiling tube reck, droppers, weight box, glass rod, measuring cylinder, measuring flask.

**Chemicals.** Ferric chloride potassium thiocyanate and potassium chloride.

**Chemical reaction at equilibrium**

$$\underset{\text{Pale yellow}}{Fe^{3+}(aq)} + \underset{\text{Colourless}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{Deep red}}{[Fe(SCN)]^{2+}}$$

**Procedure.** (*i*) Prepare 250 mL 0·1 M solution of each ferric chloride, potassium thiocyanate and potassium chloride by weighing out 6·76 g, 2·43 g and 1·86 g respectively. (Molar masses $FeCl_3.6H_2O$ =270·3 g, K SCN=97·12 g, KCl=74·5 g).

(*ii*) Pour 50 mL of $FeCl_3$ solution and 50 mL of KSCN solution into a 250 mL measuring flask with the help of a measuring cylinder. Make up the volume with distilled to a graduation mark. Shake the contents well to get a homogeneous solution of red complex.

(*iii*) Take three boiling tubes marked A, B and C. Pour 20 mL of the red complex solution obtained through step (*ii*) into each of the boiling tubes.

(*iv*) Add 5 mL of KCl solution to the boiling tube A and shake well. Keep it for reference. Now add 5 ml 0·1 M $FeCl_3$ solution to boiling tube B and 5 ml of KSCN solution to boiling tube C. Shake the contents of the tubes well.

(*v*) Now place all the tubes in the reck [Fig. 17.1(*a*]. Compare the intensisty of colours in tubes B and C to that of the reference solution A.

*(vi)* Repeat the experiment by taking another set of three boiling tubes. Now take 20 ml of the **complex** solution in the different tubes marked as D, E and F [Fig. 17.1(*b*)]. You can now add 10 ml of each of KCl, $FeCl_3$ and KSCN **solutions** to test tubes D, E and F respectively. Record your observations.

*(vii)* Also compare the intensity of colour in boiling tubes. A, B and E [Fig. 17.1(*c*)] and also in boiling tubes. A, C and F [Fig. 17.1(*d*)[. Record your observations.

**Observations**

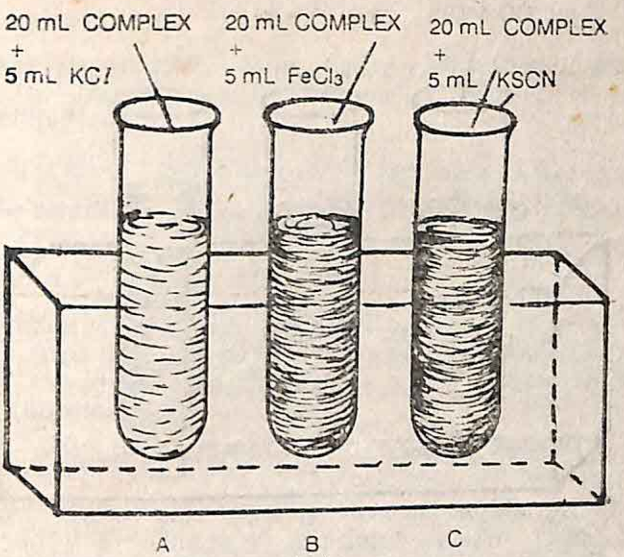
| *Boiling Tube* | *Volume added* | | | *Change in colour* | *Effect on the concentration of* $[Fe(SCN)]^{2-}$ | *Direction of shift in equilibrium observes* |
|---|---|---|---|---|---|---|
| | *KCl* (mL) | *FeCl₃* (mL) | *KSCN* (mL) | | | |
| A (Reference) | 5 | — | — | Becomes slightly lighter | Decreased | — |
| B | — | 5 | — | Deepens | Increased | Towards right |
| C | — | — | 5 | Deepens | Increased | Towards right |
| D (Reference) | 10 | — | — | Becomes lighter than A | Decreased | — |
| E | – | 10 | — | Deepens | Increased more than B | Towards right |
| F | — | — | 10 | Deepens | Increased more than C | Towards right |

**Results and Discussion**

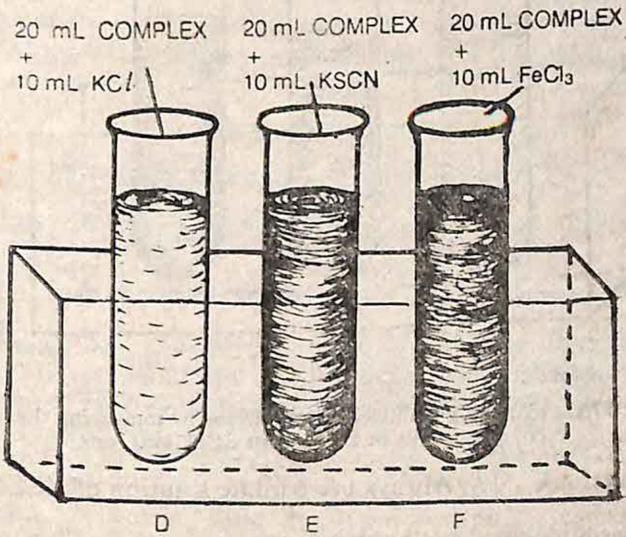
When 0·1 M $FeCl_3$ is added to an equal volume of 0·1 M KSCN solution, a red solution, (due to complex formation) is produced. The system forms an equilibrium mixture containing unreacted $Fe^{3+}$(*aq*), unreacted $SCN^-$(*aq*) and the product $[Fe(SCN)]^{2+}$. On the addition of $FeCl_3$ solution to an equilibrium solution. the colour of the solution becomes darker (deepens). A new state of equilibrium is reacted. Increasing the concentrati:n of $Fe^{3+}$(*aq*) ions has increased the concentration of $[Fe(SCN)]^{2+}$(*aq*) ions.

In the same way, the concentration of $[Fe(SCN)]^{2+}$(*aq*) also increases when a soluble thiocyanate is added to the system. Thus, an increase in the concentration of either of the reactants *i.e.*, $Fe^{3+}$(*aq*) and $SCN^-$(*aq*) ions in a reversible equilibrium shifts the equilibrium in the forward direction.

Further it has been noticed that the colour intensity in E and F is more as compared to that in B and C.


20 mL COMPLEX
+
5 mL KCl
20 mL COMPLEX
+
5 mL FeCl3
20 mL COMPLEX
+
5 mL KSCN
A
B
C

(a)


20 mL COMPLEX
+
10 mL KCl
20 mL COMPLEX
+
10 mL KSCN
20 mL COMPLEX
+
10 mL FeCl3
D
E
F

(b)

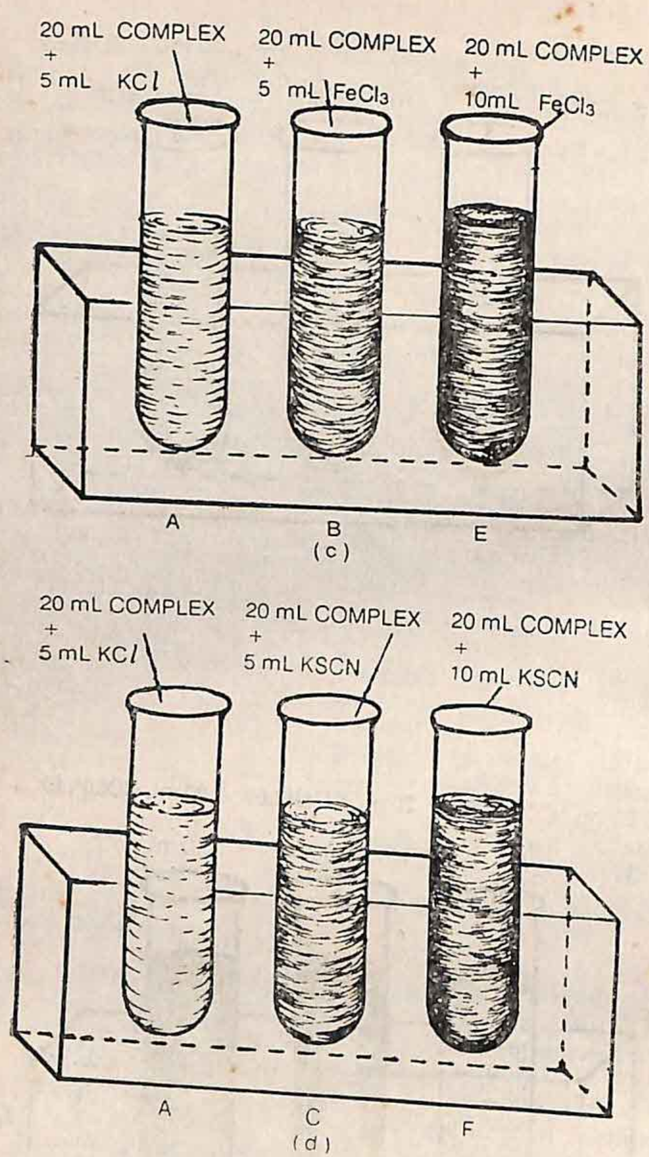

20 mL COMPLEX + 5 mL KC$l$
20 mL COMPLEX + 5 mL FeCl$_3$
20 mL COMPLEX + 10mL FeCl$_3$
A
B
E
( c )
20 mL COMPLEX + 5 mL KC$l$
20 mL COMPLEX + 5 mL KSCN
20 mL COMPLEX + 10 mL KSCN
A
C
F
( d )

**Fig. 17.1.** Changing equilibrium conditions by increasing the concentrations of $Fe^{3+}(aq)$ or $SCN^{-}(aq)$ ions,

**Precautions**. 1. Always use a dilute solution of KSCN.

(2) Select identical boiling tubes.

(3) Compare the colour intensity of the two solutions by keeping both the tubes side by side against a white back ground.

**Experiment 17.2.** To study the shift in equilibrium between $[CO(H_2O)_6]^{2+}(aq)$ ions and $Cl^-(aq)$ ions by changing the concentration of either ions.

**Apparatus.** Same as given in experiment 17.1.

**Chemicals.** Cobalt chloride, sodium chloride, sodium hydroxide.

**Theory**

A dilute solution of a cobalt (II) salt is pink in colour due to the hexadrated ion $Co(H_2O)_6^{2+}$. On the addition of HCl or metallic chlorides, the colour changes through violet to blue as the chloride ion concentration increases.

$$|\ \underset{\text{Pink}}{Co(H_2O)_6^{2+}}+4Cl^- \rightleftharpoons\ |\ \underset{\text{Blue}}{CoCl_4}\ |^{2-}+6H_2O$$

Now, if $Co^{2+}(aq)$ ions are added, blue colour gets darkened as warranted by Le Chatelier's principle. At this stage, on adding sodium hydroxide (if HCl is present) until it is neutral and aqueous solution of cobalt (II) salt (other than chloride) the colour will be regained and increasing concentration of $Co^{2+}(aq)$ ions will make the solution deep pink.

Thus, the increasing concentration of $Cl^-$ ions favours the forward reaction and the increasing concentration of $Co^{2+}$ ions favours the reverse reaction.

Now after seeking the instructions from the class teacher, the details of the experiment can be planned on the lines of Experiment 17.1.

## ORAL QUESTIONS AND ANSWERS

**Q. 17.1.** What is an equilibrium constant ?

**Ans.** It is the ratio of rate constants of two opposing reactions.

**Q. 17.2.** What is the significance of equilibrium constant ?

**Ans.** The equilibrium constant for a reaction indicates the extent of a reaction, but gives no information about the rate of reaction. It tells us how far, but not how fast the reaction goes.

**Q. 17.3.** What is effect of concentration on equilibrium constant ?

**Ans.** The numerical value of equilibrium constant, $K_c$ is unaffected by any changes in concentration of either reactants or products. With the addition of more of reactant, more of the products will tend to form, but eventually the system will adjust itself at a new equilibrium position in which the concentrations of reactants and products give the same numerical value for $K_c$.

**Q. 17.4.** Indicate an equilibrium, shift, right (forward) or left (backward), in the following reactions :

(*a*) $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)+\text{heat}$
(1) temperature is increased
(2) pressure is reduced
(3) catalyst is added

(*b*) $CO(g)+3H_2(g) \rightleftharpoons CH_4(g)+H_2O(g)-\text{heat}$
(1) temperature is lowered
(2) pressure is increased
(3) $CH_4$ is removed from the system

(*c*) $2NOCl(g) \rightleftharpoons 2NO(g)+Cl_2(g)-\text{heat}$
(1) temperature is raised
(2) pressure is increased
(3) extra chlorine gas is added

**Ans.** (*a*) (1) backward (2) backward
(3) no effect
(*b*) (1) backward (2) forward
(3) forward
(3) (1) forward (2) backward
(3) backward]

**Q. 17.5.** Does the temperature affect the value of equilibrium constant ?

**Ans.** Yes.

# Appendix

## Preparation of reagent solutions :

| *Reagent* | *Approximate normality* | *Preparation of 1 litre solution* |
|---|---|---|
| Ammonium acetate | 3 N | Dissolve 231 g in water and dilute to volume. |
| Ammonium carbonate | 4 N | Dissolve 160 g in a mixture of 140 mL of conc. ammonia and 860 mL of water. |
| Ammonium chloride | 5 N | Dissolve 270 g in water and dilute it to volume. |
| Ammonium nitrate | 1 N | Dissolve 80 g in water and dilute it to volume. |
| Ammonium oxalate | 0·5 N | Dissolve 34 g in water and dilute it to volume. |
| Ammonium sulphate | 2 N | Dissolve 132 g in water and dilute it to volume. |
| Ammonium sulphide (yellow) | 6 N | Pass $H_2S$ gas through 150 mL of concentrated ammonia solution in cold until it is saturated ; add 10 g of flowers of sulphur and 250 ml of conc. ammonia solution. Shake the mixture until the sulphur is dissolved and finally dilute with distilled water to volume. |
| Barium chloride | 0·5 N | Dissolve 61 g in water and dilute it to volume. |
| Calcium chloride | 0·5 N | Dissolve 55 g in water and dilute it to volume. |
| Cobalt nitrate | 0·3 N | Dissolve 44 g in water and dilute it to volume. |
| Copper sulphate | 0·5 N | Dissolve 125 g in about 500 mL water containing 3 ml of conc. $H_2SO_4$. Make up the volume. |
| Ferric chloride | 0·5 N | Dissolve 135 g in about 500 mL of water containing 20 ml of conc. HCl. Make up the volume. |
| Iodine solution | 0·1 N | Dissolve 12·7 g iodine in a solution containing 20 g of KI in 30 mL of and water finally dilute with water to volume. |

| *Reagent* | *Approximate normality* | *Preparation of 1 litre solution* |
|---|---|---|
| Lead acetate | 0·5 N | Dissolve 95 g in water containing conc. HCl and dilute it tovolume. |
| Mercuric chloride | 0·2 N | Dissolve 27 g in water and dilute it to volume. |
| Potassium chromate | 0·5 N | Dissolve 49 g in water and dilute it to volume. |
| Potassium ferri-cyanide | 0·5 N | Dissolve 32·5 g in water and dilute it to volume. |
| Potassium ferro-cyanide | 0·5 N | Dissolve 53 g in water and dilute it to volume. |
| Potassium iodide | 0·5 N | Dissolve 83 g in water and dilute it to volume. |
| Potassium permanganate | 0·1 N | Dissolve 3·2 g in water, dilute to volume and finally filter through glass wool. |
| Potassium thiocyanate | 0·5 N | Dissolve 49 g in water and dilute it to volume. |
| Silver nitrate | 0·1 N | Dissolve 17 g in water and dilute it to volume. |
| Sodium hydrogen phosphate | 1 N | Dissolve 120 g in water and dilute it to volume. |
| Stannous chloride | 0·5 N | Dissolve 56 g in 100 ml of conc. HCl and then dilute with water to 1 litre. Add a few pieces of tin metal. |
| Neutral $FeCl_3$ solution | | Add NaOH solution drop by drop $FeCl_3$ solution until a slight ppt. persists on shaking. Now add die HCl in drops until the ppt. just dissolves. |
| Nessler's reagent | | Dissolve 23 g of mercuric iodide and 16 g of KI in distilled water (free of $NH_3$) and dilute to 1000 ml. Then add 100 ml of 6N-NaOH solution. |

**Solid Reagents.** Aluminium powder, Ammonium chloride, Borax, Calcium chloride, Lead dioxide, Magnesium metal, Potassium nitrite, Potassium permanganate, Potassium bisulphate, Potassium dichromate, Potassium iodide, Sodium nitrate, Sodium bicarbonate, Sodium nitrite, Sodium peroxide, Sodium bisulphate, Zinc metal, Zinc chloride, α-naphthol.

**Indicators**

*Phenolphthalein solution.* Dissolve 5 g of phenolphthalein in 50 mL of rectified spirit and 500 mL water with constant stirring. Filter, if necessary.

*Litmus solution (blue)* Dissolve 10 g of the solid in 1000 mL of water.

*Litmus solution (red).* To 1% blue litmus soln. prepared above, add a few drops of HCl until the solution acquires a red colour.

*Methyl orange solution.* Dissolve 1 g of solid in one litre of hot water and filter.

*Methyl red solution.* Dissolve 1 g of solid in 0·5 litre of alcohol and dilute with water to one litre.

## International Atomic Masses

| *Element* | *Symbol* | *Atomic number* | *Atomic mass* (amu) |
|---|---|---|---|
| Aluminium | Al | 13 | 26·9815 |
| Antimony | Sb | 51 | 121·75 |
| Arsenic | As | 33 | 74·9216 |
| Barium | Ba | 56 | 137·34 |
| Bismuth | Bi | 83 | 208·280 |
| Boron | B | 5 | 10·811 |
| Bromine | Br | 35 | 79·909 |
| Cadmium | Cd | 48 | 112·40 |
| Calcium | Ca | 20 | 40·08 |
| Carbon | C | 6 | 12·01115 |
| Chlorine | Cl | 17 | 35·453 |
| Chromium | Cr | 24 | 51·996 |
| Cobalt | Co | 27 | 58·9332 |
| Copper | Cu | 29 | 63·54 |
| Fluorine | F | 9 | 18·9984 |
| Gold | Au | 79 | 196·967 |
| Hydrogen | H | 1 | 1·00797 |
| Iodine | I | 53 | 126·9043 |
| Iron | Fe | 26 | 55·847 |
| Lead | Pb | 82 | 207·19 |
| Lithium | Li | 3 | 6·939 |
| Magnesium | Mg | 12 | 24·312 |
| Manganese | Mn | 25 | 54·9380 |
| Mercury | Hg | 80 | 200·59 |
| Nickel | Ni | 28 | 58·71 |
| Nitrogen | N | 7 | 14·0067 |
| Oxygen | O | 8 | 15·9994 |
| Phosphorus | P | 15 | 30·9738 |
| Platinum | Pt | 78 | 195·09 |
| Potassium | K | 19 | 39·102 |
| Silicon | Si | 14 | 28·086 |
| Silver | Ag | 47 | 107·870 |
| Sodium | Na | 11 | 22·9898 |
| Strontium | Sr | 38 | 87·62 |
| Sulphur | S | 16 | 32·064 |
| Tin | Sn | 50 | 118·69 |
| Uranium | U | 92 | 238·03 |
| Zinc | Zn | 30 | 65·37 |

[Note. Values are based on the C—12 standard].